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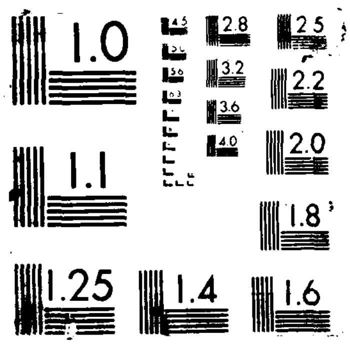
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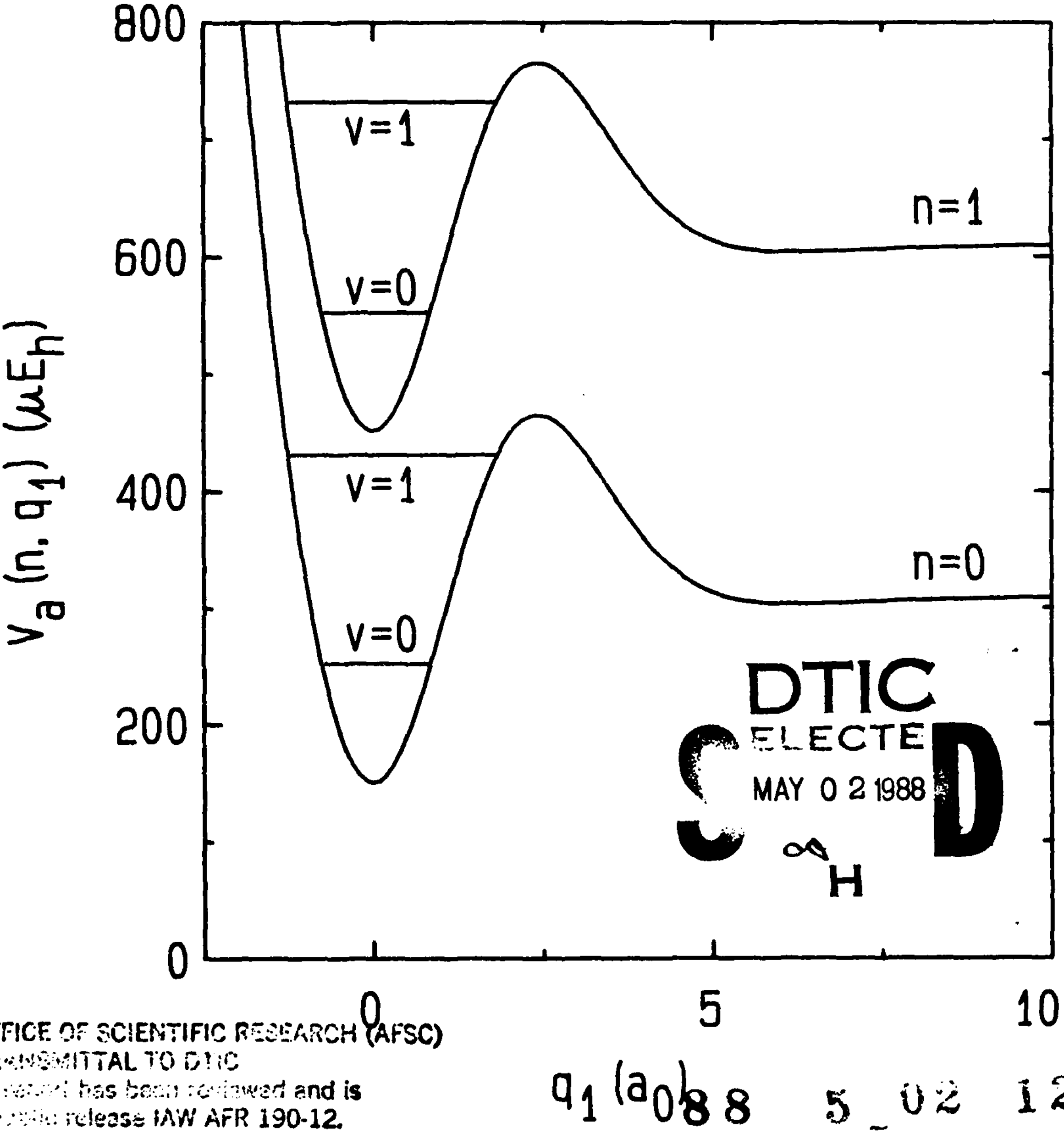
1987 American Conference on Theoretical Chemistry

Gull Lake, Minnesota
July 25-31, 1987



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The 1987 American Conference on Theoretical Chemistry was held July 25–31, 1987 at Gull Lake, Minnesota. This conference was the fourteenth in a series dating back to the 1951 Shelter Island Conference on Quantum Mechanical Methods in Valence Theory, organized by Robert S. Mulliken. In recent years the conference has broadened to include all of theoretical chemistry, and — allowing for the difficulty of classifying some papers — the 28 plenary lectures at the 1987 conference were devoted ~~approximately~~ 40% to electronic structure, 30% to dynamics, and ~~30% to~~ statistical mechanics. Lectures were typically followed by 15 minutes of plenary discussion. Special thanks goes to the session chairmen for their role in leading these discussions: Bill Goddard, Mark Child, David Chandler, Reinhold Schinke, William Miller, Pekka Pyykko, John Wheeler, Per Sigbahn, and Kenneth Jordan. In addition there were 252 official posters (plus a few unannounced ones), all of which were posted all week in pleasant, sunny rooms (and a few corridors!) to promote further discussion.

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FINAL SCHEDULE

1987 American Conference on Theoretical Chemistry
Gull Lake, Minnesota

Donald G. Truhlar, Chairman; William A. Goddard III, Vice Chairman;
John C. Tully, Vice Chairman Designate; Ernest R. Davidson, Treasurer

Sunday

5:30-9:00	Registration
7:00-9:30	Smorgasbord dinner

Monday

7:00-8:30	Breakfast
8:30-12:10	Minisymposium on Electronic Structure of Surfaces and Adsorbates.
	Discussion Leader: William Goddard
	8:30 Introduction
	9:00 Discussion
	9:15 Richard Messmer
	9:50 Discussion
	10:05 Break
	10:30 Charles Bauschlicher
	11:05 Discussion
	11:20 Dennis Salahub
	11:55 Discussion
12:15-1:45	Lunch
5:00-6:00	Poster Session A
6:00-7:00	Dinner
7:30-9:15	Session on Phase Space Dynamics.
	Discussion Leader: Mark Child
	7:30 Introduction
	7:35 Martin Gutzwiller
	8:10 Discussion
	8:25 Michael Davis
	9:00 Discussion
9:20-10:20	Poster Session B

Tuesday

7:00-8:30	Breakfast
8:30-12:10	Minisymposium on Quantum Phenomena in Condensed Phases. Discussion Leader: David Chandler 8:30 Introduction 9:00 Discussion 9:15 Peter Rossky 9:50 Discussion 10:05 Break 10:30 Bruce Berne 11:05 Discussion 11:20 Michele Parrinello 11:55 Discussion
12:15-1:45	Lunch
5:00-6:00	Poster Session C
6:00-7:30	Dinner
7:30-9:15	Session on Advances in Time-Independent Quantal Scattering Theory. Discussion Leader: Reinhold Schinke 7:30 Introduction 7:35 David Clary 8:10 Discussion 8:25 George Schatz 9:00 Discussion
9:20-10:20	Poster Session D

Wednesday

7:00-8:30	Breakfast
8:30-12:10	Minisymposium on New Techniques in Time-Dependent Dynamics. Discussion Leader: William Miller 8:30 Introduction 9:00 Discussion 9:15 Mark Ratner 9:50 Discussion 10:05 Break 10:30 Horia Metiu 11:05 Discussion 11:20 Eric Heller 11:55 Discussion
12:15-1:45	Lunch
5:00-6:00	Poster Session E
6:00-7:30	Dinner
7:30-9:15	Session I on Electronic Structure Calculations on Molecules and Reactions Discussion Leader: Pekka Pyykko 7:30 Introduction 7:35 Jan Almlöf 8:10 Discussion 8:25 Russell Pitzer 9:00 Discussion
9:20-10:20	Poster Session F

Thursday

7:00-8:30	Breakfast
8:30-12:10	Session on Phase Transitions, Interfaces, and Liquid Crystals. Discussion Leader: John Wheeler 8:30 Introduction 8:35 Ben Widom 9:10 Discussion 9:20 Daan Frenkel 9:55 Discussion 10:05 Break 10:30 Farid Abraham 11:05 Discussion 11:20 Jim Doll 11:55 Final Discussion
12:15-1:45	Lunch
5:00-6:00	Poster Session G
6:00-7:30	Dinner
7:30-9:15	Session II on Electronic Structure of Molecules and Reactions. Discussion Leader: Per Siegbahn 7:30 Introduction 7:35 Fritz Schaefer 8:10 Discussion 8:25 Rodney Bartlett 9:00 Discussion
9:20-10:20	Poster Session H

Friday

7:00-8:30	Breakfast
8:30-11:50	Session on Topics at the Interface of Electronic Structure and Dynamics. Discussion Leader: Kenneth Jordan 8:30 Introduction 8:35 Keiji Morokuma 9:10 Discussion 9:20 Bernhard Schlegel 9:55 Discussion 10:05 Break 10:20 William McCurdy 10:55 Discussion 11:05 Vincent McKoy 11:40 Discussion
11:50-1:20	Lunch

POSTER SESSIONS

There are 256 posters, to be "presented" in 8 one-hour poster sessions with 31-33 papers each. These formal presentations provide an opportunity for you to meet the author, especially if you don't know what he or she looks like. Therefore, we urge all presenters to remain at their poster for the full hour; somebody may be looking for you! Since all posters will be "up" all week though, you may also browse or discuss them with the authors at any other time that may be convenient.

Each poster has a code in the corner, e.g., 13B. The letter in the code tells the session at which the poster is to be presented. For example, poster 13B is paper no. 13 in session B.

Please notice that due to the large number of posters submitted, some of them are located in more out-of-the-way places; I am sure that their authors will appreciate it if you scout around to find all the posters.

Abstracts of the 1987 American Conference on Theoretical Chemistry

Gull Lake, Minnesota
July 25-31, 1987

The abstracts are grouped in several sections, and within each section they are arranged alphabetically by lecturer or poster presenter. The number given is the first abstract of each section and serves as a table of contents. The abstracts are followed by an alphabetical author index.

Lecture abstracts

(alphabetical)

CLASSICAL AND QUANTUM SIMULATION OF THE PHASES OF RARE-GAS ATOMS ADSORBED ON GRAPHITE

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IBM Almaden Research Center
K33/801
650 Harry Road
San Jose, California 95120

ABSTRACT:

Using classical Monte Carlo and molecular dynamics, we have studied the melting of xenon, krypton and argon films on graphite. We observe first-order melting of xenon which mimics the melting of an idealized two-dimensional film, first-order melting of krypton with the existence of an "incipient triple point,, and continuous melting of argon. All features are in agreement with laboratory experiment. The role of the graphite substrates's lateral structure on the films' melting features is emphasized. The incommensurate phase of graphite is studied using molecular dynamics with graphite substrate dimensions comparable to present-day laboratory capabilities. At low temperatures and for all coverages, honeycomb networks of domain walls are observed. The domain wall features are described as temperature is increased. The phases of He3 adsorbed on graphite are simulated using the Feynman path-integral Monte Carlo method. The fluid, commensurate solid, incommensurate solid, and reentrant fluid phases are found and are in agreement with the experimental phase diagram. The microscopic structure of the reentrant fluid is observed to be a striped domain-wall liquid.

2

ABSTRACT

Basis Set Considerations and Large Carbon Clusters

Jan Almlöf
Department of Chemistry
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Minneapolis, MN 55455

In the first part of the paper we will present our recent experience with new types of Gaussian basis sets for quantum-chemical calculations. For highly correlated wavefunctions, the use of atomic natural orbitals as basis functions has turned out to be very efficient. Large primitive basis sets can be contracted to manageable size without significant loss in correlation energy. Basis sets obtained in that way have been found to be more efficient than STO basis sets of similar size.

For calculations with a low level of electron correlation (i.e. SCF or MC-SCF) floating basis sets are advocated. Allowing the positions of the basis functions to be variationally optimized clearly requires efficient, second-order optimization techniques. The use of a floating basis reduces or eliminates the need for polarization functions. In particular, these basis sets are found extremely efficient for calculating response properties.

The second part of the paper will report calculations on large carbon clusters. Both diamond- and graphite-like structures have been investigated, the largest ones with 180 atoms (1560 basis functions). We will discuss the possibilities and limitations of such finite clusters as models for bulk diamond and graphite.

3

SINGLE REFERENCE AND MULTI-REFERENCE COUPLED-CLUSTER METHODS FOR EXCITATION ENERGIES*

Rodney J. Bartlett†
Quantum Theory Project
University of Florida
Gainesville, FL 32611

The coupled-cluster theory and its finite-order many-body perturbation theory approximations have been demonstrated to be among the most accurate approaches for the treatment of electron correlation in molecular ground states. To make applications to excited states, excitation energies, ionization potentials and related properties requires somewhat different approaches. I present several new methods within the CC framework for the evaluation of such properties. These include a CC response theory; a multi-reference method that is suited to an incomplete reference space; and an open-shell but spin-eigenfunction (RHF) single reference method. Results are presented for several molecules and compared with other methods.

*This work has been supported by the U.S. Office of Naval Research.

†Guggenheim Fellow.

4

On the bonding in transition metal systems

Charles W. Bauschlicher, Stephen R. Langhoff
Harry Partridge and Peter R. Taylor
NASA Ames Research Center
Moffett Field, CA 94035

Abstract

The computational methods required for an accurate description of the bonding in transition metal containing compounds will be described. The variety of bonding machanisms will be illustrated for selected hydrides, oxides and sulfides of the first- and second-row transition metals. Theoretical results for spectroscopic constants, dissociation energies, excitation energies, dipole moments and radiative lifetimes will be compared with the available experimental data.

5

Electrons in Polar and Non-Polar Fluids

Bruce J. Berne
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Abstract

An excess electron in clusters and bulk fluids is studied using path integral Monte Carlo techniques. The structure and spectroscopy of the excess electron is very sensitive to the polarity of the fluid and to many-body polarization forces. A novel method for determining the inhomogeneous absorption line shape is used to study solvent effects on the spectra. This method is compared with Feit and Fleck's FFT spectral method for studying the electronic states in the solvent. The host systems studied are: water, helium, and xenon.

6

ELECTRON-DIPOLE COMPLEXES

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Cambridge CB2 1EW
UK

There has been much theoretical work on the reactions of ions with molecules but theoretical chemists, in particular, have not been too keen to extend their theories to the reactions of *electrons* with molecules. One reason for this is that the problem normally requires a combined scattering and electronic structure treatment. For the exothermic reactions of electrons with dipolar molecules, however, the reaction rate is largely determined by the long-range part of the potential and theoretical techniques more typical for ion-molecule reactions can be applied. We have developed a quantum approximation for these electron-dipole reactions that includes explicitly the rotational levels of the reacting molecule. The approximation yields a simple analytical formula for the reaction rate constant and accurate close-coupling computations that we have performed confirm the accuracy of our formula. We have also managed to adapt the same theory to the "reverse" problem of the photoionisation of dipolar anions. The method is readily applicable to the prediction of relative line positions and widths for the photoionisation of systems such as H_2CCOH^- and CH_2CN^- which have recently been studied experimentally. The techniques provides a simple explanation of the interesting rotational structure observed in the photoionisation spectra for these molecules.

Bottlenecks to Intramolecular and Reactive Dynamics*

Michael J. Davis

Theoretical Chemistry Group
Argonne National Laboratory
Argonne, Illinois 60439

Bottlenecks to both intramolecular energy transfer and reaction dynamics can be defined in phase space, using ideas and techniques recently developed in the nonlinear dynamics literature. For the reactive case, these bottlenecks are consistent with the standard ones, that is transition states, when these are relevant. However, in cases where traditional methods may break down, for example, at high energy, the bottlenecks we resolve appear to be still relevant, at least for the simple systems we have studied so far. For intramolecular dynamics, there has probably not been any precise way until now to define bottlenecks to energy flow, even for the simplest systems. In this talk we discuss both types of bottlenecks. We also discuss quantum effects in the presence of the bottlenecks and extensions of the intramolecular work to larger systems.

*Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U. S. Department of Energy, under contract W-31-109-ENG-38.

8

A QUANTUM MONTE CARLO DYNAMICS

J. D. Doll, Los Alamos National Lab, MS G-738, Los Alamos, NM 87545 and D. L. Freeman, Department of Chemistry, University of Rhode Island, Kingston, RI 02881

Recently developed Monte Carlo path integral methods for the treatment of the dynamics of many-body quantum-mechanical systems will be discussed. Applications in two areas, spectroscopy and hydrogen surface diffusion, will be considered.

STRUCTURE AND DYNAMICS OF HARD-CORE MODELS FOR LIQUID CRYSTALS.

D.Frenkel
FOM INSTITUTE FOR ATOMIC AND MOLECULAR PHYSICS
P.O.Box 41883, 1009 DB Amsterdam
The Netherlands

Liquid crystals are usually not thought of as 'simple' liquids. Nevertheless, a surprising number of features of liquid crystals can be reproduced in computer simulations of very simple model systems, viz. hard ellipsoids of revolution and parallel spherocylinders. In particular, depending on the density and the shape of the hard-core particles, stable isotropic, nematic, smectic and crystalline phases are found. The existence of hard-core models for liquid crystals is important for two reasons. First of all, they can be used to test molecular theories for the static and dynamic properties of liquid crystals. And secondly, they may provide a starting point for thermodynamic perturbation theories.

These hard-core models exhibit large pretransitional fluctuations in the vicinity of some of the phase transitions, similar to those observed in real mesogens. Examples are given of the 'experimental' consequences of nematic and smectic precursor effects.

/ O

Harsh Chaos in Classical and Quantum Mechanics.

Martin C. Gutzwiller, IBM Research Center, Yorktown Heights

Classical phase space is organized into invariant tori when the system is integrable; it decays (foliates) into sheats of dimension equal to the number of degrees of freedom, where wavefunctions can be constructed. When classical chaos starts destroying the invariant tori, phase space develops all kinds of fractal structure, and classical mechanics becomes a poor basis for understanding quantum mechanics. As one reaches the extreme of "harsh" chaos, however, phase space foliates again, into stable and unstable manifolds, each again of dimension equal to the number of freedoms. Classical trajectories are naturally associated with sequences of symbols such as binary numbers or simple alphabets, as will be shown in two examples: the bound state of an electron in a donor impurity, and the scattering of an electron from a rigid molecule. Approximate wavefunctions *are hard to construct*; but energy levels and scattering phase shifts can be obtained, at least in principle, although chaos now presents us with a number of unsolved mathematical mysteries.

11

QUANTUM DYNAMICS AND QUANTUM EIGENSTATES (OR HOW THE CATERPILLAR BECOMES A BUTTERFLY)

Eric J. Heller
Department of Chemistry
University of Washington
Seattle, Wa. 98195

The subtle relationships between the nature of wavepacket dynamics on the one hand, and the character of the underlying eigenstates on the other, will be explored. This will take us into semiclassical principles, the spectrum of benzophenone, periodic orbits, and quantum ergodicity.

12

Complex Basis Set Techniques in Photoionization and Electron-Molecule Scattering Calculations

C. W. McCurdy

Department of Chemistry, Ohio State University, Columbus, Ohio 43210

There is growing evidence that the complex basis function method offers a practical way to move at least the problem of the calculation of photoionization cross sections completely into the domain of standard quantum chemical techniques. Recently, the relationship of the variational principle used in the complex basis function method to the Kohn variational princple has been established, so that a coherent picture of the use of both square-integrable and continuum complex basis functions is beginning emerge.

The total cross section for photoabsorption, as well as a variety of amplitudes in other scattering problems can be written as a matrix element of the resolvent

$$\lim_{\epsilon\to 0} (f,\ (E - H + i\epsilon)^{-1}\ g) \qquad (1)$$

with respect to functions f and g, which in the case of photoabsorption are both $\mu\Psi_0$, the dipole operator times the initial state wave function. By finding the matrix eigenfunctions satisfying

$$(\Phi_i, H\,\Phi_j) = E_i\ \delta_{ij} \qquad (2)$$

we can construct a convergent spectral approximation of the form

$$\lim_{\epsilon\to 0} (f,\ (E - H + i\epsilon)^{-1}\ g) = \sum_{i=1}^{N} \frac{(f,\Phi_i)(\Phi_i,g)}{E - E_i} \qquad (3)$$

These calculations employ a basis of complex-valued functions together with a definition of the inner product without complex conjugation. Thus the eigenvalues, E_i, appearing in the expressions above are complex as are the associated functions Φ_i.

We present results for photoionization cross sections for N_2, linear and bent configurations of CO_2, and SF_6, as well as for He and N_2 at the RPA level. These calculations easily incorporate the effects of both narrow and broad resonances. Results using continuum complex basis functions on model long and short range scattering problems will be given. The complex energy spectrum in those calculations, which are a generalized version of the Kohn method, will be plotted and the equivalence of Eq. (3) to the Kohn variational principle in this context will be explained.

13

Dynamics of Single-Photon and Resonant Multiphoton Ionization Processes in Molecules

V. McKoy, R. L. Dubs, H. Rudolph, and M. Braunstein

Arthur Amos Noyes Laboratory of Chemical Physics
California Institute of Technology
Pasadena, California 91125, USA

and

S. N. Dixit

Lawrence Livermore National Laboratory
P. O. Box 808, L-421
Livermore, California 94550

Single-photon ionization and resonant multiphoton ionization studies, which can now be carried out using synchroton radiation and pulsed dye lasers respectively, are providing important dynamical information on molecular photoionization. In this paper I will discuss some results of our recent studies of such single-photon and resonant multiphoton ionization processes in several molecules. These results will be taken from studies of (i) single-photon ionization of molecules with emphasis on the role of shape and autoionization resonances on these cross sections. Examples will be taken from both linear and nonlinear polyatomic molecules, (ii) photoionization of the oriented molecular fragments NiCO and NiN_2 as simple models of photoemission from adsorbate-substrate systems, and (iii) resonant multiphoton ionization processes in diatomic molecules. Examples will be chosen to illustrate important features in these spectra such as non-Franck-Condon vibrational state distributions; rovibrational state dependence of photoelectron angular distributions, rotational branching ratios, and circular dichroism in electric-dipole photoelectron angular distributions (CDAD) from aligned states and the use of these CDAD distributions as a probe of molecular alignment.

14

BONDING IN ELECTRON DEFICIENT MOLECULES AND SOLIDS

Richard P. Messmer
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Philadelphia, PA 19104

Abstract

Based on the computational results of recent studies using correlated wave functions (especially via the generalized valence bond approach), we have deduced a simple conceptual framework which readily explains/rationalizes bonding and structure for electron deficient systems. This conceptual framework is used to discuss some simple chemisorption problems.

15

Time Dependent Quantum Mechanics By Fast Fourier Transform Methods: Spectroscopy, Photodissociation and Thermal Rates. H. Metiu, Department of Chemistry, University of California, Santa Barbara, CA 93106.

We present applications of time dependent quantum methods to spectroscopy, curve crossing problems and thermal rate processes. This is work in its early stages and it is mostly concerned with the development and the implementation of a fast Fourier transform method. Applications are made to the dissociation of a diatomic by extremely strong IR radiation, direct computation of hot bands in electronic absorption spectroscopy, absorption spectrum of photodissociating H_3^+ including more than one excited state, and the direct time dependent calculations of thermal rate coefficients in barrier crossing and curve crossing problems. We find that the fast Fourier transform method is extremely efficient for problems with at most three quantum degrees of freedom, which are localized in space and are engaged in a short time dynamic process. The method can be extended to condensed matter problems or large molecules if the additional degrees of freedom are treated classically.

Theoretical Study on Potential Energy Surfaces and Dynamics of Electronically Excited States

Keiji Morokuma and Koichi Yamashita
Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

We discuss our recent results of the ab initio calculations on the potential energy surfaces related to the dynamics of electronically excited states. The MRSD-CI method with the DZP basis set and with effective core potentials for the second and third row atoms is used for our studies.

The first topic is the reactive scattering processes between the electronically excited Na(3P, 3D as well as 3S) atom with O_2 and HCl. The characteristics of the potential surfaces such as the barrier heights and the surface crossing between several states are analyzed and used to explain the mechanism of Na atom quenching, the electronic state selectivity of reactions and the internal energy distribution of the products.

The spectroscopy during chemical reactions is discussed as the second topic. We describe the absorption process of the K + NaCl reaction and explain the structures in the spectra in terms with the characteristics of electronic structures, potential energy surfaces and dynamics on them.

17

COMPUTER SIMULATION OF THE APPROACH TO NON-METAL TO METAL TRANSITION IN METAL-MOLTEN SALTS SOLUTIONS

A. Selloni, E. Fois, R. Car, and M. Parrinello
SISSA — International School for Advanced Studies, Strada Costiera 11, Trieste 34014, Italy

Metal molten salt solutions exhibit a rather interesting behavior as a function of concentration. In the dilute limit, the metal valence electrons are released to form F-center-like localized states that are observed in optical experiments. As the concentration increases, F-centers can interact and form aggregates, the simplest being the bielectronic complex. At even larger concentrations, transition to the metallic state occurs, accompanied by interesting phenomena such as a polarization catastrophy.

A theoretical approach to the behavior of these solutions obviously requires a correct treatment of the solvated electrons. Path integral methods have a sound quantum mechanical base and have recently provided considerable insight into the problem of very dilute solutions. However, these methods cannot explore dynamical properties and face serious difficulties in handling the Pauli exclusion principle in the many electron case. We show here that a different approach based on local spin density functional theory can overcome some of these difficulties and provide a powerful tool for the study of Born-Oppenheimer time-dependent processes in many-electron systems.

We present results for a variety of concentrations: these calculations help to elucidate the complex physical phenomena occurring in these systems as they approach the non-metal to metal transition. The overall agreement with experimental data proves the reliability of our approach which is of general interest, and can be employed to study other physical systems.

18

Electronic Structure of Heavy-Atom Molecules

Russell M. Pitzer
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The Ohio State University
Columbus, OH 43210

Developments over the last few years have made ab-initio electronic-structure calculations, using the core-potential approximation, feasible on polyatomic molecules containing heavy atoms. The spin-orbit effect is also treated in this approximation, and both kinds of integrals can now be done effectively. Double-group theory results are used, when sufficient spatial symmetry is present, to make the Hamiltonian matrix real even though the wavefunction is not. Greatly improved computational capacity is, of course, also a key factor.

The PuF_6 and $U(C_8H_8)_2$ (uranocene) complexes are used as examples. Both have, to a first approximation, two non-bonded 5f electrons and therefore 91 wavefunctions with reasonably low energy. The excitation energies depend on the strengths of the spin-orbit, electron repulsion, and ligand interactions. Higher-lying states have ligand-to-metal charge transfer character.

/ 7

Mean-Field Methods for Vibrational Energetics and Molecular Dynamics

Mark A. Ratner
R.B. Gerber

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Northwestern University
Evanston, IL 60201

Abstract

Mean-field methods offer several advantages for theoretical description of molecular energetics and dynamics; these include convenient physical interpretation, unified treatment of energy level structure and energy flow dynamics, and validity in both the strong and weak-coupling regimes of interactions between modes. The lecture will describe recent developments in both the time-independent Self-Consistent-Field and Time-Dependent Self-Consistent-Field versions of the approach. The time-independent SCF developments include: (1) Inversion of the vibrational energy spectrum to yield a highly accurate, full stretching-bending potential for CO_2; (2) A distorted-wave approach to vibrational predissociation of vdW molecules, based on SCF states as zero-order initial states; (3) An anharmonic version of Slater theory for predissociation of vdW clusters based on SCF states. The advances in TDSCF that will be presented are: (1) A linearized TDSCF approximation that offers advantages both in treating time evolution and in calculating the energy spectrum through a Fourier space approach; (2) A time-independent, random-phase approximation for vibrational dynamics, closely related to (1), and applicable to vdW predissociation dynamics; (3) TDSCF quantum calculations of overline lineshapes (application to CH_3-C≡CH); (4) A new approach to classical TDSCF, based on using the classical analogue of a (time-dependent) wavefunction; (5) Comparison between quantum TDSCF and exact time-dependent quantum calculations on dissociation of I_2Ne.

20

Structure and Spectroscopy of the Hydrated Electron

Peter J. Rossky
Department of Chemistry
The University of Texas at Austin
Austin, Texas 78712

ABSTRACT

A combination of classical liquid state simulation techniques, path integral sampling, and quantum chemical methods have been used to examine various aspects of the state of the hydrated excess electron in a molecular sample of room temperature liquid water. Specific aspects to be addressed in the talk include: (1) the void structure of pure liquid water and its potential role in initial localization of excess electrons; (2) the equilibrium electronic and solvation structure of the hydrated electron; and (3) the calculation and characterization of the optical absorption spectrum of the solvated species.

TRANSITION METAL CLUSTERS AND THEIR INTERACTIONS WITH ATOMS AND MOLECULES: THE LOCAL DENSITY FUNCTIONAL DESCRIPTION. Dennis R. Salahub, Département de Chimie, Université de Montréal, C.P. 6128, Succ. A, Montréal, Québec, H3C 3J7, Canada.

The Local - (Spin) - Density methods incorporate exchange and correlation effects through a local correlated electron gas potential. A Gaussian representation of the wave functions, coupled with a (relativistic) model potential for the core electrons, allows the accurate calculation of the electronic and magnetic structure, geometries, and vibrational properties of medium sized transition metal clusters (up to a dozen or so atoms) interacting with adsorbates. A compact, orbital, description of the bonding is obtained. Following a brief description of the method, I will discuss recent results on transition metal clusters and on their interactions with adsorbates. Some of the following topics will be discussed:

- Chemisorption and diffusion of CO on Pd clusters.
- Hydrogen chemisorption on and diffusion through clusters of Pd and Rh.
- Hydrogen interacting with Pd-Sn alloy clusters - implications for catalysis.

22

1987 American Conference on Theoretical Chemistry

The Coupled Cluster Single and Double Excitation (CCSD) Model: An Assessment

Henry F. Schaefer III

Department of Chemistry
University of California
Berkeley, California 94720

Abstract

The recent development of the analytic gradient technique for the CCSD method allows an assessment of the reliability of this method. Comparisons with various configuration interaction (CI) methods and with experiment will be made.

23

Quantum Reactive Scattering Studies of Heavy-Light-Heavy Reactions

George C. Schatz

Department of Chemistry

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This talk will discuss the use of two rather different quantum mechanical methods for describing reactive collisions involving the transfer of a light atom between two heavy atoms.

The first method is the coupled channel distorted wave (CCDW) approach, in which the scattering matrix is expressed in terms of matrix elements of H-E between scattering wavefunctions obtained by solving coupled channel equations for nonreactive scattering in the reagent and product arrangement channels. Although this is a perturbative method, it is capable of high accuracy for reactions at energies where tunnelling is important. Results of an application to Cl + HCl done in collaboration with B. Amaee and J. N. L. Connor[1] will be discussed.

The second method involves the use of a new hyperspherical coordinate coupled channel reactive scattering code. In this code, three different sets of coordinates are used to define basis functions so that the "matching" between internal and asymptotic solutions can be reduced to one-dimensional quadratures involving subspaces of the full basis. Comparison with results for $H + H_2$ demonstrate that the method is numerically exact when fully converged. Results of applications to Cl + HCl will be discussed.

1. G. C. Schatz, B. Amaee and J. N. L. Connor, Chem. Phys. Lett. 132, 1 (1986); Comp. Phys. Commun., submitted; J. Phys. Chem., to be published.

a/4

An Improved Algorithm for Reaction Path Following

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A new algorithm is presented for obtaining points on a steepest descent path from the transition state down toward the reactants, and down toward the products (if mass-weighted coordinates are used, the path corresponds to the intrinsic reaction coordinate). Points on the reaction path are found by constrained optimizations involving all internal degrees of freedom of the molecule. The points are optimized so that the segment of the reaction path between any two adjacent points is given by an arc of a circle, and so that the gradient at each point is tangent to the path. The resulting reaction path is continuous, differentiable and piecewise quadratic. Because the segments of the path are arcs of circles, this method is capable of following very curved reaction coordinates. Consequently, the present scheme can use much larger step sizes than previous algorithms. The method has been tested on the following reactions: $HCN \rightarrow CNH$, $SiH_2 + H_2 \rightarrow SiH_4$, $CH_3 + H_2 \rightarrow CH_4 + H$, $F^- + CH_3F \rightarrow FCH_3 + F^-$, and $HF + C_2H_4 \rightarrow C_2H_5F$. Reaction paths calculated with a step size of 0.3 au are almost identical to those computed with a step size of 0.05 au.

25

Interfacial Structure and Tension in Model Phase Equilibria

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Some theoretical models of phase equilibria and the associated interfaces are reviewed. Included are Ising and extended-Ising lattice models, and continuum models, treated mostly in mean-field approximation. The models describe normal liquid-vapor interfaces, the interface between liquid helium and its vapor near the λ-point, the orientation of amphiphiles at surfaces, the structure and wetting properties of the interfaces in microemulsion phase equilibria, and the composition profiles of the three-phase line, and accompanying line tension, in three-phase equilibrium with non-vanishing contact angles. The vanishing of the surface tension at critical points and tricritical points is also discussed.

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Poster abstracts

Electronic structure of surfaces and adsorbates

(alphabetical by name of presenter,
which is underlined)

1H

Abstract of poster to be presented at the 1987 American Conference on Theoretical Chemistry, Gull Lake, Minnesota, 27-31 July 1987.

"ATOMIC AND MOLECULAR CHEMISORPTION ON AG CLUSTERS"

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ABSTRACT

Oxygen and chlorine (as well as alkali metals) play central, but unresolved, roles in the Ag-catalyzed olefin epoxidation reaction. In order to sort out the mechanistic steps involved in this process, we have examined the interaction of relevant adsorbates with Ag clusters as models for Ag aggregates present on actual supported catalysts. Using ab initio generalized valence bond (GVB) wavefunctions as starting points for dissociation-consistent CI (configuration interaction) calculations, we have predicted preferred binding sites, geometries, vibrational frequencies, and binding energies for O, Cl, H, O_2, OH, and C_2H_4 on Ag clusters. For example, this work suggests the existence of two near-degenerate states of $O_{(ad)}$, each with a binding energy of 78 kcal/mol (in excellent agreement with TDS data), but only one predicted to be active for olefin epoxidation. Implications for other aspects (e.g. the role of promoters) of this reaction are discussed.

This work was partially supported by the Shell Development Company, the Shell Companies Foundation, the International Precious Metals Institute, and the National Science Foundation.

1B

CLUSTER APPROACH TO STRUCTURE OF SURFACES AND CHEMISORPTION

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The electronic structure of small transition metal particles is studied in the local density approximation, using a discrete variational method for solving the self-consistent field equations. Both free particles and clusters embedded in a medium representative of an (hkl) face of an infinite crystal are described. Energy levels and charge and spin densities are analyzed to obtain information about the intermetallic bond and to make comparison to photoelectron, optical, and X-ray absorption data. Bader's topological density analysis scheme is used to explore bond linkages and the structure of "deformed atoms" within the clusters.

Binding energies are calculated using the statistical total energy expression and used to study equilibrium geometries and fragments of the interatomic potential surface. Molecular dynamics techniques employing the embedded atom scheme are used to couple classical theory to the electronic densities derived from first principles. Surface relaxation and reconstruction of (hkl) crystal faces are described in this approach.

The approach and interaction of a few simple molecules such as H_2, C_2H_2, and NO with free particles and simulated surfaces is described in the self-consistent framework. Differential changes in binding energies, interatomic bonding, and spectral distributions are presented for comparison with thermal desorption, vibrational, photoelectron, and electron diffraction data. The use of X-ray near edge absorption spectra as a fingerprint for adsorption site is facilitated by calculated K- and L-edge photoabsorption cross-sections.

1C

Local Space Approximation for Treatment of Chemisorption - Hydrogen Atom(s) on a Model Transition Metal

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ABSTRACT

The local space approximation (LSA) for the treatment of chemisorption is explored using a single hydrogen atom as well as a pair of hydrogen atoms adsorbed onto a cubium model transition metal substrate. Electron repulsion is taken into account through the Anderson-Newns approximation to the unrestricted Hartree-Fock Hamiltonian. Convergence with respect to the size and shape of the local space is studied and compared to that of the corresponding finite cluster. Both the charge and spin density waves are analyzed. We also show how to find adsorbate-induced surface states by means of the LSA technique.

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1D

Ab Initio Studies of Cesiated Beryllium*

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It has recently been reported that the deposition of Cs on a wafer of Be metal results in the reduction of the work function of Be by 2.3 eV.[1] In this work, the system is modeled as a cylindrical 'plug' from a cesiated Be wafer having a radius that includes a one unit cell step along the a direction. Ab initio restricted open-shell Hartree-Fock calculations are carried out in which effective core potentials (EP) are used to represent electrons in the 1s subshell of Be and those in the 1s-4s, 2p-4p, and 3d-4d subshells of Cs. The Be-Be internuclear distances are fixed at the bulk metal values with one and three Cs atoms positioned in various orientations on the ends of the plug. Cs-Cs and Cs-Be distances are optimized in SCF calculations. Specific stoichiometries include up to 33 Be atoms and 6 Cs atoms. Binding energy, ionization potential, excitation energies, Mulliken populations, and second moments of charge are calculated for each system and compared to the results of a recent study on naked Be clusters.[2]

[1]G.S. Tompa, M. Seidl, W.C. Ermler and W.E. Carr, Surf. Sci., in press.
[2]R.B. Ross, W.C. Ermler, C.W. Kern and R.M. Pitzer, Chem. Phys. Lett., in press.

*Work supported in part by the National Science Foundation and the U.S. Air Force Office of Scientific Research.

/E

Core-valence correlation effects on cluster-adsorbate interactions.

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A one-electron description of metal atoms (e.g. Ni, Cu) has been developed for use in cluster studies of chemisorption and reactions at metal surfaces. The core-electrons (including the 3d shell) are described using an ECP with the large 3d relaxation modelled using an attractive level- shift operator. Very good agreement is obtained with all-electron calculations on smaller clusters, such as Ni_5O, Ni_5H and Cu_5O. However, both in the ECP and all-electron calculations the bond distance of the adsorbate to the surface is considerably too long compared with experiment. This is also true for larger clusters.

A possible source of this error is neglect of core-valence polarization and correlation effects. To investigate the importance of these effects and to improve the description of the 3d relaxation we have included the effective core polarization potential of Mueller et al [1] in SCF, CASSCF and CI treatments of the clusters with adsorbates. Results will be presented from all-electron and ECP calculations on some Cu and Ni clusters with oxygen and hydrogen adsorbates. The importance of these additional interactions will be discussed.

1. W. Mueller, J. Flesch and W. Meyer, J.Chem.Phys. **80**,3297(1984).

1F

Modeling Graphite with Ab initio Calculations of Carbon Clusters

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Small clusters of carbon atoms have been investigated as possible models for graphite. Two-dimensional clusters which may serve as models for the graphite basal plane are emphasized in the study. *Ab initio* restricted Hartree-Fock calculations, using a double-zeta basis set, have been used for the study. Calculated values for the work function, valence band width, π-band width, cohesive energy, and net charge densities for the ground states of each of the clusters are presented and compared with experiment.

16

Models for chemisorption on nickel and copper surfaces.

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Accurate models for studying chemisorption on nickel and copper surfaces have been developed. Based on results from all-electron calculations on smaller clusters, one-electron ECP's for the metal atoms are developed which account for the important 3d relaxation effects. Using these ECP's, CI calculations are done on larger clusters with up to 50 atoms. Core-valence correlation effects are incorporated through a special operator (see separate poster). For oxygen chemisorption, correlation effects on the adsorbate and the adsorbate-substrate bonds are shown to contribute more than half of the chemisorption energy. Results are obtained which agree with available experiments for both hydrogen and oxygen atomic chemisorptiom on nickel and copper. The chemisorption of atomic carbon, nitrogen and oxygen is compared. The dissociation reactions of H_2 and O_2 are studied over different sites on Ni(100) and Cu(100). H_2 dissociates without a barrier on nickel but with a barrier on copper. O_2 dissociates without a barrier on nickel. Different molecularly chemisorbed states are identified.

1H

The Electronic Structure of Nickel Clusters

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1. Introduction; A quite number of investigations has been performed on the transition metal clusters because of industrial as well as scientific interests. In this report, the electronic structure of Ni clusters will be discussed by using ab initio SCF and CI calculations. The problem to be discussed is whether the electronic structure of Ni clusters resembles that of the solid or not. Only the results of SCF are shown for saving space. The linear, triangular(D_{3h}), square planar(D_{4h}), square pyramid(C_{4v}), and bisquare pyramid(O_h) are assumed for Ni_{2-6}. The bond distance for the nickel clusters is 4.71 a.u.

2. Band Structure from Koopmans' Theorem; Band structure given by the Koopmans' theorem for Ni_n is shown in Table 1 together with the results of symmetry broken (S.B.) SCF calculations. The band width is obtained by the difference of the highest occupied and lowest occupied orbital energies. The Fermi level is defined as the the highest occupied orbital energy. Top of the d band relative to that of the s band is also given in the eighth column of the table. The Fermi level is composed of a $(4s)^{-1}$ state. The top of the d band is far below the Fermi level irrespective of the cluster size as shown in the table. On the other hand the Fermi level of the solid is composed of the $(4s)^{-1}$ and $(3d)^{-1}$ states, showing that the electronic structure of the small Ni clusters predicted by the Koopmans' theorem is far different from that of the solid.

Table 1 Band structure for Ni_n (eV)

	Koopmans' theorem							S.B.
	d band			s band			top of	top of
	LO	HO	width	LO	HO	width	d band	d band
Ni_1	-12.5	-12.5	0.0	-6.4	-6.4	0.0	-6.1	0.4
Ni_2	-14.7	-10.5	4.2	-6.2	-6.2	0.0	-4.3	1.1
Ni_3	-15.2	-10.8	4.4	-7.6	-4.4	3.2	-6.4	0.0
Ni_4	-15.0	-10.4	4.6	-8.1	-5.4	2.7	-5.0	0.5
Ni_5	-15.8	-11.1	4.7	-9.6	-5.1	4.5	-6.0	0.1
Ni_6	-16.1	-11.5	4.6	-10.5	-5.7	4.8	-5.8	0.0

3. Band Structure from Symmetry Broken ΔSCF; If one uses the Koopmans' theorem for the ionization of 3d electrons, resulting d hole is distributed over the whole cluster which consists of symmetrically equivalent atoms. We, however, noted that the d electron is very localized at the atom. We have performed S.B. SCF calculations for Ni_2 - Ni_4 where the localization of the d electron at one of the constituent atoms is allowed, if the state is energetically lower. The resulting d hole is localized as expected and the Fermi level is composed of top of the d band or those of the s and d bands as shown in the last column of Table 1. We have estimated the levels of $(3d)^{-1}$ for Ni_5 and Ni_6. The Fermi level again consists of the $(3d)^{-1}$ and $(4s)^{-1}$ states. As a whole, so far as the position of the d band concerns, the electronic structure of the small Ni clusters resemble that of metal.

2 H

Abstract for the 1987 American Conference on Theoretical Chemistry

Local Density Functional Theory of Chemisorption: Cu and Ag on Si(111) Surfaces

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In this contribution, the interactions between single Cu and Ag atoms with a Si(111) surface are investigated using local density functional theory. The surface is represented by a cluster consisting of 20 Si atoms and 26 H atoms saturating the bonds towards the bulk. For all Si atoms, d-functions are included in the numerical LCAO basis set. Total energy calculations reveal the three-fold hollow position as the energetically most favorable adsorption site for both Cu and Ag. In this geometry, the noble metal atoms interact with the dangling bonds of three nearest neighbor Si atoms as can be seen from the atom-projected local densities of states. For Cu, marked d-contribution to the bonding is found, whereas this effect is less pronounced for Ag, in agreement with experimental evidence. The Si back-bonding is significantly reduced by Cu, in contrast to Ag. Furthermore, the results shed new light on a controversy concerning the adsorption geometry of Ag atoms on a Si(111) surface.

Theoretical Studies of the V^{+2} Ion in Fluoride Crystals*

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Divalent vanadium substituted into weak field fluoride crystals is an example of a 'phonon-terminated' four-level laser with the emission terminating on vibrationally excited levels of the ground electronic state. MgF_2:V^{+2} has been considered as an attractive laser-gain medium for use in high-average power laser drivers for fusion applications.[1] Laser action at a wavelength of 1.12 μm (8915 cm^{-1}) was reported by Johnson et. al.[2] as early as 1966. We have carried out *ab initio* electronic structure calculations on the ground and excited states of MgF_2:V^{+2} in order to better understand the nature of the ground and excited state absorption and the nonradiative processes that effect the laser performance. These theoretical studies represent one of the most accurate calculations of the optical spectrum of an ion/host system to date. The calculated position of the zero-phonon line corresponding to the origin of the $^4T_2(B_2)$ absorption band was found to be in error by only 2-3%. Similar accuracy was obtained for the peak of the $^4A_2 \rightarrow {}^4T_2$ absorption. As determined from the calculated potential energy curves, the predicted peak of the $^4T_2 \rightarrow {}^4A_2$ emission at 9195 cm^{-1} is in error by only ~275 cm^{-1} (3%), which is consistent with the magnitude of the agreement for the zero-phonon line but opposite in sign. Vertical ESA transitions from the $^4T_2(B_2)$ state to the crystal field split components of the $^4T_{1a}$ state were calculated at 6682, 6984, and 8535 cm^{-1} and at 18234, 18482, and 19451 cm^{-1} for transitions to the components of the $^4T_{1b}$ excited state. After correcting these excitation energies for the errors found by comparing the calculated and observed ground state absorption, we obtain good agreement with experiment.

References

1. W. F. Krupke, *V:MgF_2 Solid State Laser for Fusion Applications*, in Proc. Intern. Conf. on Lasers '80 (New Orleans, La., 1980)
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3. 1981 Laser Program Annual Report, Lawrence Livermore National Laboratory, Livermore, Calif., UCRL-50021-81 (1982), p 7-94; 1982 Laser Program Annual Report, Lawrence Livermore National Laboratory, Livermore, Calif., UCRL-50021-82 (1983), p 7-78.

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Poster abstracts

Phase space dynamics

(alphabetical by name of presenter, which is underlined)

Highly excited large amplitude motion vibrational levels of triatomic molecules (HCN/HNC): A novel quantum approach

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We have developed[1,2] a novel, efficient and accurate variational quantum method for the calculation of highly excited vibrational levels of triatomic molecules. The method is particularly well suited for applications to "floppy" molecules, as well as molecules which can isomerize. The large amplitude motion (LAM) coordinate is discretized via the discrete variable representation (DVR).[1,2] The remaining degrees of freedom are represented by the distributed (real) Gaussian basis (DGB),[1,2] contracted to a small eigenfunction basis at each of the discretized values of the LAM coordinate.

Using the above DVR-DGB approach we have performed[2] the first accurate quantum calculations of the LAM vibrational (J=0) levels of HCN/HNC (all modes are included), lying above the isomerization barrier. Some of the levels are extensively delocalized over both HCN and HNC local minima. Our analysis shows that for HCN/HNC the threshold for significant delocalization is determined by the height of the vibrationally adiabatic bending barrier. The nearest neighbor level spacing distribution resulting from the calculations suggests that for this potential surface,[3] and in the energy region considered here (up to ~15000 cm^{-1}), HCN/HNC behaves largely as a regular system.

Re-organization of the vibrational Hamiltonian to a (truncated) representation of adiabatic bend eigenvectors and its use for the calculation of the vibrational levels of polyatomic molecules, as well as extensions to J>0 cases, will also be presented.

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[1]Z. Bačić and J. C. Light, J. Chem. Phys. **85**, 4594 (1986).
[2]Z. Bačić and J. C. Light, J. Chem. Phys., in press.
[3]J. N. Murrell, S. Carter, and L. O. Halonen, J. Mol. Spectrosc. **93**, 307 (1982).

Phase changes and phase space transitions in small clusters

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ABSTRACT

The power spectrum of the velocity autocorrelation function in molecular dynamics simulations yields information concerning the regularity of the motion in the phase space for a given system. In molecular dynamics studies of the melting transition in small clusters, for example, several transitions are observed in the power spectra in passing from the normal mode, solidlike limit to the nonrigid, liquidlike limit. The Grassberger and Procaccia algorithm[2] has been employed to obtain estimates of the fractal dimension (ν) and Kolmogorov entropy (K_2) for the N=3 argon cluster at several energies along the caloric curve. Changes in the ν and K_2 values with increasing energy are discussed in relation to qualitative changes in the power spectra in order to relate the solidlike-liquidlike phase change to the observed phase space transitions. The scaling curves are found to give quantitative measures of both the transition from normal mode to coupled oscillator behavior and the degree of separability of vibrational and rotational motions for the Ar_3 cluster. At energies where passages between the equilateral triangle potential wells occur (and diffusion in the power spectrum), a partial separation of length scales is observed in the scaling curves for chaotic motion within the equilateral triangle potential well versus the lower dimensional reaction coordinate for passage between wells. Thus, the dimension calculations may provide a new means of characterizing the transition state in classical calculations. The entropy appears to decrease along the well-defined coordinate for interwell passage.

[1]T.L. Beck, J. Jellinek, and R.S. Berry, J. Chem. Phys. (July 1, 1987).

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Algebraic quantization to arbitrary order in $\hbar$

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The method of algebraic quantization is an accurate and efficient means of calculating vibrational eigenvalues for multidimensional potentials. In this approach, the classical Hamiltonian is simplified, using canonical transformations, to produce a function of action variables and resonant combinations of angles. This simplified classical Hamiltonian is then turned into a quantum operator, using a quantization rule. Although there are many possible quantization rules, the accuracy of the resulting semiclassical eigenvalues is dependent upon the rule actually used. We give a method for including higher-order corrections in $\hbar$ which is applicable to any invertible quantization rule. The addition of these corrections reduces the dependence of the method on the quantization rule used. Furthermore, it allows quantum effects to be incorporated into a problem in a controlled manner. For a polynomial Hamiltonian, the series of corrections truncates. Thus, algebraic quantization applied to polynomial Hamiltonians can be made to converge to its quantum analog, Van Vleck perturbation theory, by introducing sufficiently high powers of $\hbar$, giving results which are entirely independent of quantization rule. Several systems are quantized using the method; it is found that including higher order corrections in $\hbar$ can lead to substantial improvement in energy eigenvalues. The method can also be used to produce wavefunctions; preliminary results will be presented.

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*Alfred P. Sloan Fellow

2F

THE DIVIDED PHASE SPACE OF THREE COUPLED OSCILLATORS

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The phase space of a system of three nonlinearly coupled harmonic oscillators is examined and shown to consist of three distinct regions.

We use a two-dimensional representation of the phase space in which surviving KAM tori correspond to unique points. Fourier analysis of low energy trajectories started on this plane reveals an intricate network of resonances (the Arnold web). The intersections of these resonances are thin stochastic layers that contain long periodic orbits. Several high-order periodic orbit approximants to the three-degree-of-freedom analog of the golden mean torus have been found in such layers. Three-dimensional space-of-section plots illustrate the coherent organization of tori and provide evidence for the existence of a new type of isolated orbit having only one integer relationship between its angle-action frequencies.

At higher energy, a substantial region of chaos develops around one of the three fundamental periodic orbits of the system. The boundary of the region, which separates large-scale regular from large-scale chaotic motion appears as a sharp line in our representation. Examination of the relative rates of randomization of the chaotic trajectories reveals another boundary that is less well resolved. Trajectories there remain trapped for long but finite periods of time. This second boundary may play a role similar to that of the Cantorus in two-degree-of-freedom systems. Arguments are given as to the origin of both surfaces.

A Periodically Forced Oscillator Model of Van der Waals Fragmentation: Classical and Quantum Dynamics

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Abstract

A one degree of freedom, periodically forced Hamiltonian is shown to describe much of the relevant classical dynamics observed in earlier studies of a two degree of freedom model for HeI_2 fragmentation. The simplicity of the forced oscillator model permits easy, but thorough numerical investigation of the quantum dynamics of fragmentation using an accurate wavepacket propagation method. Quantum dynamics results are compared with classical dynamics results based on both the usual quasiclassical procedure for selecting initial conditions and on the Wigner distribution. The exact Wigner distribution as a function of time is obtained from the quantum dynamics results and very interesting, unexpected parallels with the classical phase space structure are evident.

2H

Adiabatic Switching: Molecular Bottlenecks

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A time independent adiabatic switching algorithm for the calculation and construction of inter and intramolecular bottlenecks will be presented. This algorithm has been applied to a variety of systems. These include HeI_2, H_2O and the Ford-Walker Hamiltonian. The calculations which will be discussed provide significant insight to the structure of phase space in the chaotic regions.

DYNAMICAL SIMULATION OF NONCONSERVATIVE SYSTEMS: A GENERAL SCHEME*

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We consider the problem of simulation of dynamical behavior of physical systems under conditions different from those corresponding to the microcanonical ensemble. A generalization of the isothermal molecular dynamics scheme suggested recently by Nose [J. Chem. Phys. 81, 511 (1984); Mol. Phys. 52, 255 (1986)] is presented and it is shown that already the original Hamiltonian of Nose implies many different dynamics each of which can, in principle, simulate a canonical ensemble. In addition we prove that in fact any Hamiltonian of an extended system consisting of the physical system and a "bath" (the latter is represented by a single dimensionless coordinate and its conjugate momentum) can produce dynamical time-averages of physical quantities equal to their canonical ensemble averages. This is achieved by appropriately scaling the time for trajectory propagation. The implication of time scaling on the phase space distribution generated by a dynamics is clarified and an invariance feature of the ergodicity property under the time-scaling transformation is established. The fact that more than one dynamics can generate the same phase space distribution for a physical system suggests an indicative test of ergodicity of these dynamics. In fact infinitely many different dynamics can mimic the same ensemble-averaged behavior of a physical system. This opens the possibility of selecting a dynamics which would furnish not only the desired averaged quantities but would describe adequately detailed dynamical phenomena, such as relaxation and time-correlation properties, as well. This possibility should also allow for choosing dynamics appropriate for simulating systems under specific realistic (e.g., experimental) conditions. Finally, a procedure is outlined for dynamical simulation of any generalized statistical ensemble.

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ALGEBRAIC FITTING OF CHAOTIC SPECTRA

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It can be argued that spectral energy levels in the classically chaotic regime are intrinsically unassignable, in the sense that the meaning of chaos in a quantum system is that all approximate quantum numbers are lost. This would seem to indicate that detailed fitting of individual levels as traditionally performed by spectroscipists is impossible. We investigate whether it is nonetheless possible to fit a chaotic spectrum with a suitably defined algebraic Hamiltonian. This requires a wide extension of the methods traditionally used by spectroscopists for nonlinear least squares fitting of rotation-vibration spectra. A fit with anharmonic normal modes and a coupling term such as Darling-Dennison or Fermi resonance is a single resonance approximation and therefore corresponds semiclassically to quasiperiodic motion. The invariant torus for such motion corresponds to the restricted "polyad" basis used by spectroscopists in these fits. In contrast, a complete fit of a chaotic spectrum requires an infinite number of resonances in the complete bound state basis. We investigate a method to bypass these problems in two ways. A limited number of leading resonances are used to achieve a sparse matrix Hamiltonian. This results in a small number of parameters that need to be varied independently in the fit. A systematically truncated basis is also used to make the matrix diagonalizations tractable. Results are presented of nonlinear least squares fits of "experimental" test systems consisting of model coupled anharmonic oscillators. Fits of systems with a moderate degree of chaos are investigated, and also systems with global chaos and a Wigner distribution of levels. The novel information about highly excited, highly anharmonic regions of the potential surface that can be obtained from such fits is also investigated.

3C

[Abstract for 1987 American Conference on Theoretical Chemistry]

Atomic Electrons in Strong Magnetic Fields: Semiclassical Description of the Transition Regime.

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Abstract

A semiclassical treatment of a one-electron atom in a strong, static magnetic field B is employed to generate the energy spectrum in the "transition regime". The Hamiltonian for the system in cylindrical coordinates (z, ρ) is

1. $H = (p_z^2 + p_\rho^2)/2m - k/r + L_z^2/2m\rho^2 + \lambda\rho^2$

where L_z is the z component of the anglular momentum, k the nuclear charge parameter, $\lambda = e^2B^2/8mc^2$. A coordinate transformation reduces dependence to a single parameter, $\hat{L} = L_z/\alpha\beta$, with $\alpha = (k/8\lambda)^{1/3}$, $\beta = m^{1/2}k^{1/3}(8\lambda)^{1/6}$. At $\hat{L}_T = 7^{1/2}\ 3^{1/6}/2$, the character of the lowest energy trajectories changes abruptly from elliptical to helical. The bifurcation of regular trajectories into two families in the "transition regime" near $\hat{L}_T$ can be related to the 2:1 resonance which occurs at $\hat{L}_T$. An analysis based on the Mathieu equation relates the boundary between the motions to the stable and unstable behavior of the "Floquet solutions". Generation of composite surfaces of section by integration of classical trajectories confirms the analysis.

A standard SOS method based on classical trajectories leads to the determination of the action $\hat{J}_z$ by quadrature. The total phase is computed by a variation on the trajectory close method which relies on counting the number of trajectory cycles at each point on the SOS. The second action, $\hat{J}_\rho$, is then found from $S = \hat{J}_z + 2\hat{J}_\rho$, and non-integer quantum numbers obtained in the usual fashion: $(N_q + 0.5)2\pi = \alpha\beta\hat{J}_q$. A two-dimensional interpolation to integer quantum numbers provides the separate sets of energy eigenvalues for each of the two classes of regular motion supported by this potential. The dependence of the energies on the parameter $\hat{L}$ displays the behavior of the semiclassical eigenvalues as the system passes through the avoided crossing at the resonance. We find that as $\hat{L}$ increases the elliptical states disappear and helical states appear; however, the helical state may appear before or after the elliptical state which it replaces has ceased to exist.

3 D

Intramolecular Bottlenecks and the Phase Space Structure of Planar OCS: Characterization of Chaotic Dynamics in Multidimensional Systems

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A detailed investigation of nonstatistical behavior and long time correlations in the classical dynamics of planar OCS near its dissociation energy is presented. By performing fast Fourier transform analysis of sequential segments of long trajectories, the local fundamental frequencies of chaotic motion can be determined. We demonstrate that the evolution of frequencies from segment to segment can be used to characterize important dynamical features of planar OCS, such as long time trappings around multidimensional resonance zones and the passage through phase space bottlenecks. It is shown empirically for this system that three degree of freedom bottlenecks to intramolecular energy flow are associated with pairwise irrational golden mean frequency ratios, and that large energy exchange between zeroth order modes is accompanied by passage of one or more local frequency ratios through "noble" values related to the golden mean. For limiting collinear configurations, the phase space structure correlates with the results of previous work by Davis on collinear OCS. This two degree of freedom structure is found to persist in the full three dimensional problem. In addition, several features specific to multidimensional systems have been identified in the planar OCS phase space.

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3E

A PHASE SPACE ANALYSIS OF THE COLLINEAR I+HI REACTION

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We have studied the collinear I+HI reaction using an approach based on concepts of nonlinear dynamics. It is found that many aspects of the classical reaction dynamics may be understood in terms of simple phase space structures. For example, the formation of long-lived reactive complexes is identified with passage into a well defined closed region of phase space bounded by a separatrix created by the manifolds emanating from the outer PODS. We can calculate the probability of complex formation by computing the flux across this phase space dividing surface. We find that this formation probability oscillates as a function of energy. Reactivity sectors are constructed in the interaction region from the homoclinic oscillations of a separatrix. The oscillating reaction probability observed in the I+HI reaction is explained by the pattern of overlap of different homoclinic oscillations as a function of energy. An analysis of the effect of separatrix crossing on the validity of the vibrationally adiabatic approximation has been carried out.

3F

Secondary Encounters in Collinear, Dissociative Atom-Diatom Collisions

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Classical trajectory simulations of dissociative collisions between a diatomic molecule A_2 and an atom M have shown that the correction κ_3 for recrossing of an appropriately chosen phase space dividing surface is independent of temperature T when collisions are dominated by A-M repulsion. Recrossing in this case is thought to be due to secondary A-M encounters in the course of a collision, but the physical basis of the T-independence of κ_3 has been unclear. As a first step toward providing such a basis, collinear classical trajectories were run for several of the same three body potentials and mass ratios that had been studied in the three dimensional simulations. Recrossing corrections derived from the collinear trajectories show a T behavior similar to that of κ_3. The collinear results can be interpreted in terms of the single encounter impulsive collision model with a simple modification to account for secondary encounters.

3G

Investigation of Scaling Behavior Relevant to Unimolecular Dissociation

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Recently the concept of intramolecular and intermolecular bottlenecks centered in phase space has been used to model the dynamics of unimolecular reactions. The previous work is based on recent advances in non-linear dynamics. The goal of the present study is to expand on the earlier work for T-shaped HeI_2 molecule, specifically to derive rate laws. The determination of rate laws is dependent on the ability to characterize the trends of relevant quantities as a function of energy. It is with this goal that the scaling behavior of dynamical quantities is investigated.

These studies utilize easily applied techniques for systematically calculating relevant quantities using action principles. Spatial scaling, area of the interaction regions and the flux across the intermolecular and intramolecular bottlenecks are all investigated. The destruction of quasi-periodic regions due to period-doubling is also studied.

Work supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under contract W-31-109-ENG-38.

3H

Interaction of Molecular Rotation with Large-Amplitude Internal Motions: A Rigid Twister Model of Hydrogen Peroxide

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The classical dynamics of the interaction between molecular rotation and hindered internal rotation is studied for a "rigid twister" model of hydrogen peroxide, H_2O_2. The rigid twister model is obtained from an adiabatic separation of the torsional motion from the remaining 3N-7 small-amplitude vibrational modes. A two degree of freedom rotation-torsion Hamiltonian is obtained using the Augustin-Miller canonical transformation to express the three molecule-fixed components of the total angular momentum **j** in terms of the magnitude, j, the component along the body fixed z-axis, k, and χ, the angle conjugate to k. Surfaces of section are employed to characterize the phase space structure of the model Hamiltonian. Regions of quasiperiodic, resonant quasiperiodic, and chaotic rotation-torsion motion are identified and correlated with the nature and extent of rotation-torsion energy transfer. Our results demonstrate the possibility of substantial energy transfer between rotation and torsion. Implications of our findings for the rotational dependence of the unimolecular decay of overtone excited hydrogen peroxide and for the general problem of interaction of rotations with large-amplitude internal motions are discussed.

a) Mathematical Sciences Institute Fellow.
b) Alfred P. Sloan Foundation Fellow.

4A

THEORETICAL STUDIES OF THE ADDITION AND DISSOCIATION REACTION: H + CO ⇌ HCO

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RRKM calculations of the thermal addition and dissociation rate constants are carried out on the Harding surface (*J. Chem. Phys.* **1986**, *85*, 911) for HCO. Structures, frequencies and energetics at the stationary points on the surface are presented for HCO and DCO. Due to the relatively weak H-CO bond (bond energy of about 16 kcal/mole) and the few degrees of freedom in HCO, the spacing between the vibrational states of the metastable HCO* is quite large. This motivates a form of RRKM theory in which metastable HCO* is explicitly considered to exist only at isolated vibrational resonance energies and all addition and dissociation dynamics is controlled by these isolated resonance states. The rate constant calculations focus on both the implications of this isolated resonance model and the comparison to available thermal rate constant measurements.

Among the major implications of this model are (1) a standard treatment of tunneling can *not* be included in the calculations, (2) explicit summation over total angular momentum *must* be included in the calculations, and (3) measurable recrossing effects are predicted in the approach to the high pressure limit of the rate constants.

The calculations are compared to the addition rate constant measurements of Michael, et al (*J. Chem. Phys.* **1972**, *57*, 3736) and Dorfman, et al. (*J. Chem. Phys.* **1973**, *59*, 5199) and the recent direct dissociation rate constant measurements by Gutman, et al. Both the barrier height $V^{\ddagger}$ and $\langle \Delta E \rangle_{tot}$, the average energy transfer between metastable HCO* and the buffer gas, were varied for optimal agreement. The final calculated rate constants fall within the error bars of all the measured values. The final value of $V^{\ddagger}$ is 1.5 kcal/mole, consistent with many other addition reactions. The final value of $\langle \Delta E \rangle_{tot}$ varies between -40 to -50 cm^{-1} for buffer gases N_2, H_2, He, and Ar, lower than that typically measured for larger metastable molecules. The calculations are used to extend the measured dissociation rate constant to combustion temperatures. The resulting rate constant is then fit to a modified Arhennius expression for inclusion in modeling studies.

Time-independent exact quantum scattering calculations are in progress to characterize the isolated resonance states approximated in these calculations. Preliminary results have been published by Bowman, et al.(*J. Chem. Phys.* **1986**, *85*, 6225). Comparisons between the RRKM calculations and these and other results will be presented.

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Poster abstracts

Quantum phenomena in condensed phases

(alphabetical by name of presenter,
which is underlined)

4 B

Charge Distribution and Energy Levels of Interstitial Ti in Silicon.

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In our study of the interaction of transition metals with semiconductors [1,2], we have investigated interstitial Ti in silicon at the SCF + limited CI level. The silicon host is represented by a $Si_{30}H_{40}$ cluster. This cluster is centered around a tetrahedral interstitial site. It consists of two shells of Si atoms: the first shell contains 10 atoms, at $R_c = 4.4 - 5.1$ bohr from the central interstitial site, the second contains 20 atoms, at $R_c = 8.5 - 8.9$ bohr. The Ti atom is in the center of the cluster. Hydrogen atoms serve as saturators of the dangling bonds. The effect of the Si core electrons is represented by an effective potential, using the method of Pettersson et al. [3].

The ground states of interstitial Ti, Ti^+ and Ti^{2+} are $^3T_1(\text{---}t_2^4)$, $^4A_2(\text{---}t_2^3)$ and $^3T_1(\text{---}t_2^2)$, respectively. The partially occupied t_2 orbitals mainly consist of transition metal (TM) 3d orbitals. However, they are much more delocalized than in the free ions. E.g., the sphere around Ti, containing 95% of the open shell (t_2) density has a radius of 8 bohr for neutral Ti in $Si_{30}H_{40}$, compared to 5 bohr for free Ti ($3d^4$, av. of states). The total impurity-induced electronic charge, however, is well localized, due to the response of the (Si) closed shell density, which compensates for the open shell delocalization. This is an illustration of the so called dual nature of TM impurities in semiconductors [4]. Ionization of the impurity, Ti $\rightarrow Ti^+$ and $Ti^+ \rightarrow Ti^{2+}$, causes an efficient "self regulating response" of the Si cluster: only 10% of the electron hole is in the impurity region ($R_c < 4$ bohr), 25% is between the two shells of Si atoms and the major part is beyond the outer shell of Si atoms ($R_c > 10$ bohr).

Finally, we compare the results for Ti in $Si_{30}H_{40}$ with those for Ti in $Si_{10}H_{16}$, the cluster employed in a previous series of calculations [1,2]. The charge distribution in the central part of the two clusters is very similar. All TM associated (d-d like) excitation energies decrease with 10% when $Si_{10}H_{16}$ is replaced by $Si_{30}H_{40}$. Impurity associated ionization energies decrease considerably, due to the extra relaxation offered by the additional shell of 20 Si atoms

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4C

The Role of the Solvent-Solute Interaction in Vibrational Population Relaxation in Diatomics

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We have investigated the vibrational population relaxation of the lowest ($1 \rightarrow 0$) vibrational transition for Br_2 in a dense Ar fluid. The method of calculation is a mixed quantum-semiclassical-classical simulation procedure. The adiabatic wavefunctions and the energies for the vibrational states and the non-adiabatic coupling between vibrational states are obtained from perturbation theory for fixed values of the rotational and translational variables. The relaxation rate for the vibrational transition is evaluated using a semiclassical surface hopping theory of non-adiabatic processes. The configurations of the rotational and vibrational variables are sampled from a classical canonical ensemble density using standard Monte Carlo sampling. We discuss the dependence of the relaxation rate on various forms of the solvent-solute interaction and the masses of the solvent and solute particles. The role of the force constant and the frequency of the diatomics and the effects of temperature and pressure are also studied.

4-D

Second-Quantized MTGLE: Applications to Boson and Fermion Systems

by

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A new second-quantized molecular timescale generalized Langevin equation (MTGLE) theory will be described and applications to both boson and fermion systems will be presented. The theory is applicable to nonlinear Hamiltonians and to the strong coupling case. A definition of a quantum bath will be given. The effect of a pulse disturbance in the primary zone will be shown to dissipate at long times as the full system returns to equilibrium.

4E

Renormalization Group Approach to Electronic Structure of Atoms and Molecules#

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We introduce a set of methods to elucidate the nature of chemical bonds in atoms and molecules based on renormali-zation group (RG) techniques and ideas from lattice gauge field-theory. The many fermion quantum mechanical problem is recasted as a functional-integral formulation on a lattice in space and imaginary time. We introduce RG transformations that project out the core electrons but retains information about the "low energy" valence electrons. Computer simulation algorithms are developed for non-perturbative calculations of valence electron proterties.

We will discuss (a) results from a hybrid molecular dynamics and MC algorithm for simulations of lattice fermion systems; (b) a new method for canonical ensemble MC fermion simulation; (c) a transfer matrix optimized configuration expansion for finding the ground states of lattice Hamiltonian; (d) a complete set of wave functions (for a free particle) that are exponentially localized in both position and momentum space, and (e) RG techniques in the presence of bound states in the potential.

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#In collaboration with K.G. Wilson, J. Wilkins and S. White of Cornell University

4F

Classical-Quantum Correspondence in Vibrational Relaxation of Nonlinear Systems: A Model Calculation

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Relaxation of a strongly nonlinear system coupled to a dissipative bath is studied classically, by direct numerical integration of dissipative equations of motion, and quantum mechanically, by solution of the corresponding master equation. The primary system consists of kinetically coupled local-mode Morse Oscillators, a well-known model for stretch-stretch interaction in H_2O. The phase space of this system contains large local mode (nonresonant) and normal mode (1:1 resonance) regions.

When dissipation is present, good classical-quantum correspondence is found in the local mode region, but there are qualitative differences between classical and quantum results in the normal mode region. Classically, normal mode states relax to other normal mode states, while quantum-mechanically they convert to extreme local-mode states which subsequently relax. This conversion can be described as incoherent tunneling through a dynamical barrier. A classical nonlinear resonance analysis gives a physical picture of the relaxation dynamics. This analysis is readily generalized to more realistic dissipation models.

4G

Abstract of paper for the
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Chemistry, Gull Lake, MN,
July 26-31, 1987

Calculation of Reaction Rates and Kinetic Isotope Effect for Dissociative Chemisorption of H_2 and D_2 on Ni(100), Ni(110), and Ni(111) Surfaces

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We have applied canonical variational transition state theory with multidimensional semiclassical transmission coefficients to examine the dynamics of the dissociative chemisorption of H_2 and D_2 on the (100), (110), and (111) faces of a Ni crystal and to calculate rate constants for these reactions. We have used the modified four-body LEPS potential energy surface of Lee and DePristo [J. Chem. Phys. **85**, 4161 (1986)] in which the diatom-surface potentials are represented by effective medium theory plus empirical pairwise interactions. For the (100) face of Ni, we found that the lowest energy dissociative chemisorption process occurs over the bridge site with a small classical barrier of 2.8 kcal/mol. Dissociative chemisorption of the molecule over a center site yielding atoms on long-bridge sites of the (110) face is found to have a negligible barrier (0.06 kcal/mol). For the (111) surface, we found that the classical barrier to dissociation is 3.2 kcal/mol. At low temperatures, tunneling is far more important in the dissociation of H_2 and D_2 on the (100) face than on the other two low-index faces of Ni. However, zero point energy contributes significantly to the kinetic isotopic effect on all three faces, and the ratios (k_{H_2}/k_{D_2}) between the rate constants for dissociative chemisorption of H_2 and D_2 at 100, 150, 300, and 800 K, respectively, are: 15.3, 7.2, 2.8, and 1.8 on Ni(100); 2.4, 1.8, 1.5, and 1.4 on Ni(110); and 3.3, 3.1, 2.8, and 2.0 on Ni(111).

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4-H

Delocalization and Correlation Effects in Atomic Systems: The Hubbard Model for General Spin

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Delocalized states and energy bands for atomic particles in periodic potentials necessarily arise when we consider the motion of atoms at low temperatures on crystalline surfaces and in solids. The situation is significantly different from electronic motion in periodic potentials however, because of i) the large differences in mass and inter-particle interactions, and ii) different statistics, when bosonic species are considered.

We have used the Hubbard model[1] to analyze the effects of interatomic correlations and quantum statistics on the delocalization and transport of bosons of spin 0 and 1, in two-dimensional periodic potentials, and have compared these to the behavior of fermions of spin ½. These statistics are appropriate to diffusion of atomic hydrogen on metals at low temperatures[2]. We use a periodic cluster technique to solve exactly for the eigenstates of certain selected symmetries, over a range of values of U/W, the ratio of the on-site repulsion, U, to the single particle bandwidth, W. The delocalization of the ground state is studied as a function of the cluster size and symmetry, of U/W, of the particle statistics, and of coverage. The periodic cluster technique enables us to obtain the exact many-body states for a discrete set of reciprocal points, and hence to look at the behavior at high coverage where a description in terms of single particle states fails[3].

Implications for the two-dimensional diffusive motion of atoms adsorbed on crystalline surfaces are discussed.

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Poster abstracts

Time-independent quantal scattering theory

(alphabetical by name of presenter,
which is underlined)

5/7

DYNAMICS OF ELEMENTARY CHEMICAL PROCESSES: THE REACTION RADIUS APPROACH

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The quasi separability of the radius of the hyper-spherical formulation has been shown to provide an important alternative to the concept of reaction path in the theory of chemical reaction rates. (CPL 93 (1982) 174; 93 (1982) 179; J.Mol.Struct.Theochem. 93 (1983) 319; 107 (1984) 95).

In this paper, recent adavances in formal aspects of the hyperspherical coordinate approach to the n-body problem (JCP 76 (1982) 1587; 81 (1984) 3355; 85 (1986) 1355; 85 (1986) 1362) are exploited for generalizing to 3-D results previously limited to collinear reactions. Basic orthogonal trajectories of the potential energy surfaces are individuated to be the valley bottom and the ridge lines: their dependence on the total angular momentum is studied, rigorous bounds are provided.

The appearance of angular momentum barriers in the effective valley bottom line is shown by examples to be responsible for long lived states in unimolecular decay and in photodissociation.

The association of nonadiabatic effects to the ridge lines is stressed: In particular the role of the ridge as the separatrix between modes is pointed out (CPL 110 (1984) 43). Procedures to deal with these features are developed for the adiabatic and the sudden limiting cases, which are explicitly worked out and tested towards exact model results. Finally, the incorporation of transition state ideas is outlined: In particular, the RRKM assumptions of energy randomization in unimolecular decay are discussed within this formulation.

PREDISSOCIATION DYNAMICS OF H_3^+

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Carrington and Kennedy [1] have published a vibrational predissociation excitation spectrum of H_3^+ by CO_2 laser absorption which contains 27,000 lines corresponding to final state lifetimes of 10^{-7}-10^{-9}sec and which shows four clear peaks in low resolution. How should such highly excited states be modelled, what factors allow such long lifetimes, what types of optical transition are involved, how can the spectral density and the low resolution structure be understood, and why for example does HD_2^+ predissociate mainly to H^++D_2, rather than D^++HD.

A simultated spectrum derived from a model of angular momentum H^+/H_2 complexes with a linear dipole along the H^+/H_2 axis will be presented [2,3]. Intensity borrowing from a $\Delta\ell = 1$ progression in orbital excitation of the H^+ around H_2 is the main source of oscillator strength. The observed lifetime range can be explained only by tunnelling. The estimated state density (one state per 30cm^{-1}) and the number of states with the relevant lifetime (10 per total angular momentum for each parity block) accounts for the number of observed lines if saturation is assumed (as indicated by recent experiments, [4]).

Aspects of the predissociation of HD_2^+ will also be reported.

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5C

The role of resonances in the theory of laser-induced excitation transfer

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The theory presented here is an extension and revision of our recent analysis of laser-induced excitation transfer (LIET).[1] It is applicable to atomic collision processes represented schematically by the equation

$$A(i) + B(i) \longrightarrow [(A(i)\cdots B(i)) \xrightarrow{\hbar\omega} (A(f)\cdots B(f))]$$

$$\longrightarrow \begin{bmatrix} A(f) + B(f). \\ A(i) + B(i) + \hbar\omega'. \end{bmatrix}$$

The laser frequence ω is assumed not to be resonant with any electronic transition of the atoms A and B. Thus, the presence of photons is important only during the brief interval when the two atoms interact. As indicated the atoms are initially in a composite internal state i and collide to produce a complex $(A(i)\cdots B(i))$. This intermediate may undergo stimulated adsorption of one or more laser photons to produce a second excited complex $(A(f)\cdots B(f))$. This intermediate may simply dissociate, yielding the isolated atoms $A(f) + B(f)$ as *products of the collision*. However, if the complex $(A(f)\cdots B(f))$ is bound, it cannot dissociate but will eventually decay back to the ground electronic state i. This may occur with the spontaneous emission of a photon, giving the products $B(i) + \hbar\omega'$. Because of this the cross section is a strong function of the laser frequency and exhibits a series of resonances. Other studies of LIET (or closely related processes) are available, but we are aware of no fully quantal treatment incorporating the effects mentioned above. Perhaps the most closely related studies are those of Julienne and Mies,[2] and Regenorter and Feautrier,[3] who have studied the fluorescence produced by the products of collision systems.

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3 D

Abstract of a paper for the
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$\mathcal{L}^2$ Amplitude Density Method for Atom-Molecule Rearrangement Collisions

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A new method has been developed for the quantum mechanical calculation of chemical reaction rates, and it is being applied to reactive collisions of H, D, O, Br, and F with H_2 in either the ground or first excited vibrational state. The method involves solving a set of coupled integral equations equivalent to the Schroedinger equation with scattering boundary conditions by expanding the reactive amplitude density in a square-integrable basis set. Both the method of moments and a variational method have been implemented. These methods reduce the computational work involved in the problem to two steps: the numerical evaluation of multidimensional integrals and the solution of large sets of linear equations. Our program is designed for and run on a Cray-2 computer, and it takes advantage of its large memory and vector processing ability. The results obtained so far are very encouraging and have already helped to clarify disagreements between more approximate theoretical results and experimental results. Selected details of the methods and results for two or more systems will be presented in the present poster, and the reader's attention is also directed to a second poster by Zhang et al. presenting results for the exothermic H + HBr $\leftrightarrow$ H_2 + Br reaction.

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INVESTIGATIONS WITH THE FINITE ELEMENT METHOD

5E

The collinear A + BC (A,B,C=H,D,Mu) and $F+H_2$ reaction

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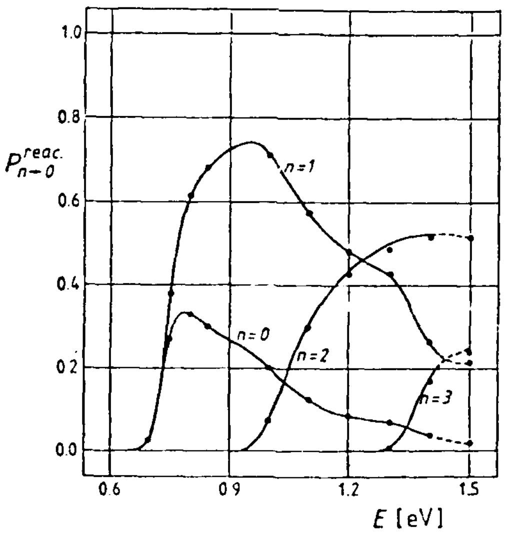
Abstract. We are investigating systematically the use of the finite element method (FEM) for solving the Schrödinger equation. The following work is devoted to the calculation of vibrational transition probabilities for the collinear reactive system A + BC (i.e. $H + H_2$ and their isotopes and $F + H_2$). The calculations are full two-dimensional as in the early work of Askar et al./1/ and the results are compared with the conventional basis set expansion methods using the R-matrix or S-matrix propagation.

We made extensive analysis of FEM on the vector-computer Cyber 205 and developed a vector code for the efficient use in two dimensions, so that in the near future applications even in three dimensions will be possible.

For the hydrogen isotope reactions we investigated the following combinations: a) $H + H_2$ b) H + DH,D + HD and H + MuH , symmetric reaction c) D + HH, H + DD und Mu + DD,asymmetric reaction. We calculated the transition probability for five open vibrational channels and found excellent results compared to the known "exact" values.

The details of our FEM calculations are the following /2/: The symmetry of the potential surface was not used in case of a symmetric reaction in order to have a good comparison to the values of an asymmetric reaction. This results naturally into a larger number of grid points. The integration area was discretized into triangles where we defined quadratic polynomials for the local wavefunction. With this simple ansatz convergent results can be reached for most reactions with $\approx$10000 grid points, even in the case of $F + H_2$.

As an example in fig.1 we show our results for the reaction probability of $Mu + D_2$ (n = 0,1,2,3) $\longrightarrow$ MuD (n' = 0) + D. The lines are results of Bondi et al. /3/ and the dots are the present results.



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5F

ANALYTIC EXPRESSION OF THE PHASE SHIFT IN TERMS OF THE POTENTIAL FOR ELASTIC COLLISIONS.

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Abstract

The canonical functions method for the solution of the Schrödinger equation for elastic collisions is considered. The derivation of the partial wavefunction ψ_l for a given potential V(r) and a given energy E in terms of the canonical functions $\alpha(r_0;r)$ and $\beta(r_0;r)$ on one side, and the use of the ψ boundary conditions on the other side, lead to an analytic relation between the phase shift δ_l and the canonical functions α and β : $tg(Kr_0 - l\pi/2 + \delta_l) = -K\beta(r_0;0)/\alpha(r_0;0)$ where $K^2 = 2\mu E/\hbar^2$ and r_0 is a "large" arbitrary origin. This expression has the following advantages : i) It implies the use of the canonical functions α and β, and not of the wavefunction ψ, so it is free from the initial value problem (the initial values of α and β are : $\alpha(r_0;r_0) = \beta'(r_0;r_0) = 1$, $\alpha'(r_0;r_0) = \beta(r_0;r_0) = 0$) ; ii) It is a relation between δ_l and the potential V (since α and β are given in terms of V) ; iii) It can be simplified by taking $r_0 = (1/2 + n) K$ (with n = 1, 2, ...), it becomes : $tg\,\delta_l = -K\beta(r_0;0)/\alpha(r_0;0)$. Examples of the numerical applications to the collision (e - H) and the collision (H_2 - H) considered by many authors are presented and discussed.

56

A Lanczos Reduced L^2 Method for the Direct Quantum Evaluation of Thermal Rate Constants

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Miller[1] gave an exact quantum formulation for the thermal rate constant in terms of the time integral of the flux-flux autocorrelation function across a surface dividing reactants from products:

$$K(T)Q \equiv \int_0^{\infty} C_f(t)dt$$

$$C_f(t) = tr\{Fe^{-\gamma H} Fe^{-\gamma^* H}\}$$

$$\gamma = \frac{1}{2kT} - \frac{it}{\hbar}$$

$$F = \frac{1}{2m}\,[\delta(S)\,p_s + p_s\,\delta(s)]$$

where K is the rate constant, Q the reactant partition function, S=0 the dividing surface, and H the Hamiltonian. We use a localized representation;distributed Gaussian basis[2] or discrete variable representation[3] near S=0 and evaluate the above expressions by Lanczos reduction and matrix Lanczos propagation, i.e. the eigenvectors of F with non-zero eigenvalues (a small set) are determined by Lanczos reduction. This set serves as the initial set for a matrix Lanczos time propagation.[4] The rate constant can then be evaluated by diagonalization of the reduced Hamiltonian and analytic integrations.

Results for 1-D systems and collinear reactive $H+H_2$ scattering will be presented. Progress on 3-D reactions will be reported.

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5H

Laser-assisted ionization in He*($2^1S, 2^3S$) - He(1^1S) collisions

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Much attention is currently being directed toward experimental and theoretical investigations of inelastic atomic collisional events that take place in the presence of strong laser fields. Processes which involve photoabsorption by a colliding pair of atoms are called "laser assisted." These are events which would not occur if the laser were turned off. An example is provided by a recent experimental study[1] of the laser-assisted Penning Ionization processes

$$\mathrm{He}^*(2^1S, 2^3S) + \mathrm{He}(1^1S) + \hbar\omega \longrightarrow \mathrm{He}^+(1^2S) + \mathrm{He}(1^1S) + e^-$$

The photon energies ($\hbar\omega$ = 3.49 eV and 3.53 eV) used in these experiments were less than the photoionization threshold of either of the metastable reactants He*(2^1S) or He*(2^3S). Furthermore, the power density of the laser was maintained at a level low enough to ensure that no multiphoton events would occur.

Our report is devoted to the theory of these laser-assisted chemi-ionization processes and to our current numerical investigation of the corresponding cross sections. Among the several attractions which have drawn us into this study is the relative simplicity of helium compared with the alkali atoms to which most previous experiments have been devoted. Much already is known,[2] both experimentally and theoretically, about the excited state helium-helium potential energy surfaces. Furthermore, the computation of the relevant matrix elements involving electronic wave functions is far less demanding for this system than for any other and the results are thus apt to more reliable.

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QUANTUM REACTIVE SCATTERING IN THREE DIMENSIONS
USING HYPERSPHERICAL (APH) COORDINATES

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ABSTRACT

Accurate coupled channel calculations of quantum reactive scattering in three physical dimensions (3D) using Adiabatically adjusting Principal axis Hyperspherical coordinates are reported for both zero and nonzero total angular momentum J and for systems both with symmetric ($H+H_2$) and unsymmetric ($D+H_2$) mass combinations. This approach opens a way to accurate 3D reactive scattering calculations for heavier systems and higher energies than before possible.

6/3

Rotational state distributions following direct photodissociation of triatomic molecules

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We examine product rotational state distributions following the direct photodissociation of a triatomic molecule. Full close-coupling and classical trajectory calculations are performed for a model system which is characteristic of strong translational-rotational coupling. The product state distributions are determined by the rotational reflection principle, which was recently established by us.[1] It is believed to describe qualitatively many measured distributions. The main subject of this study is the test of classical trajectory methods. Generally good agreement between the quantal and the classical calculations is obtained if the initial motion of the parent molecule is represented by a quantal distribution function. However, in some cases the classical results are seriously in error. The origin of this failure can be traced back to some peculiar trajectories. We also test the applicability of a classical distribution function for the initial state and conclude on the basis of our model that this can not be recommended.

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6C

Abstract of a paper for the
American Conference on Theoretical
Chemistry, Gull Lake, MN,
July 26-31, 1987

Completely $\mathcal{L}^2$ Golden Rule Method for Resonance Energies, Widths and Branching Ratios

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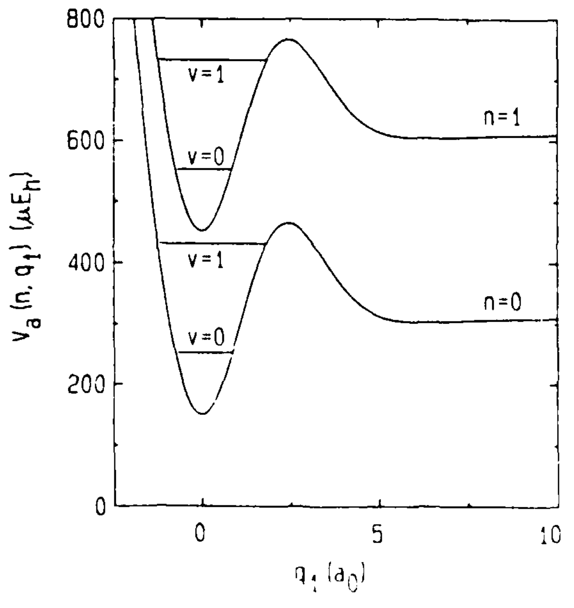
Abstract. We have calculated resonance energies and widths for both one- and two-dimensional scattering resonances by a general method involving only Hamiltonian and overlap integrals in a single square-integrable basis set containing a scale parameter. We use a stabilization method with a compactness criterion to find the resonance energies and a generalization of the golden rule formalism to calculate the widths. For one-channel resonances we have found good agreement with accurate resonance energies and widths obtained by Breit-Wigner fits. Preliminary results on two-channel resonances indicate that we can calculate branching ratios to similar accuracy.

This work was supported in part by a research grant from the National Science Foundation, by the Minnesota Supercomputer Institute, and by an NSF Graduate Fellowship to S.C.T.



Vibrationally adiabatic potential curves for the two-dimensional model of the vibrational predissociation of a van der Waals complex. The horizontal lines denote the bound-state and quasibound-state energies of the adiabatic curves. The n=1, v=1 state is a two-channel resonance that can decay into either the n=1 or n=0 continuum.

6D

Abstract Submitted to the
1987 American Conference on Theoretical Chemistry

R-Matrix Propagation Applied to the Reactive Scattering of H + H_2 and its Isotopic Analogs

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We extend the earlier work[1] in our group on the reaction of H+H_2 to higher energies and to six reactions in the H_2D and HD_2 isotopic systems. R matrix propagation techniques are generalized to asymmetric systems with modifications of the matching surfaces, propagation in the match region, and the use of the discrete variable representation to accurately describe the vibration-rotation interaction. The results appear insensitive to changes in coordinate systems and basis expansions. Preliminary results for seven reactions for J=0 through 1.50 eV have been published[2], and more accurate results will be given. Work is in progress on these reactions for higher angular momentum partial waves from which differential cross sections and anisotropy parameters will be calculated. Results will be presented for the accurate theory, and several approximate treatments will be touched upon including the centrifugal sudden approximation.

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2. Frank Webster and J. C. Light, J. Chem. Phys. **85**, 4744-4745 (1986)

Abstract of a paper for the American
Conference on Theoretical Chemistry
Gull Lake, MN, July 26-31, 1987.

6E

Quantum Mechanical Calculation of the Three Dimensional Br + H_2 Reaction

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ABSTRACT

The first accurate quantum calculation on the Br + H_2 reaction in three dimensions using the L^2 Amplitude Density Method is reported. Reactive probabilities have been computed for the total angular momentum J=0, and for total energy from 0.19eV to 0.45eV. The final results are very well converged with respect to basis set and various numerical parameters. The computed exchange reaction probabilities of H + BrH --> HBr + H are compared to these of another calculation which neglected the hydrogen abstraction reaction (H + BrH --> Br + H_2).

March 30, 1987

Poster abstracts

Time-dependent dynamics

(alphabetical by name of presenter, which is underlined)

6F

Energy Dependence of the Photodissociation Dynamics of Ionic Clusters: A Simulation Study of $Br_2^-Ar_n$

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The size dependence of dynamical effects in cluster reactions is now more easily studied for cold ionic clusters in supersonic beams than for neutrals because mass selection of parent ions can be performed without excessive fragmentation. Recent experiments on the photodissociation dynamics of ionic clusters such as $Br_2^-(CO_2)_n$ have shown dramatic changes in caging behavior as a function of cluster size [1]: weak caging (small caging fraction) occurs for n<11 while strong caging (caging fraction ≈ 1) sets in at n=12. Based on minimum energy structures and MD simulations of the photodissociation of $Br_2^-Ar_n$ these experimental observations have been explained in terms of two caging mechanisms: for large n, the kinetic cage effect operates, while for small n (n<8) relatively strong ion-induced dipole forces give rise to an attractive cage effect [2].

In this work we present results of MD simulations of the photodissociation ($X\ ^2\Sigma_u^+ \rightarrow {}^2\Pi_g$) of $Br_2^-Ar_n$ as a function of photon energy. The ion-induced dipole contribution to the energy is treated in a self-consistent manner using a point charge/point dipole approximation with 1/2 electron on each Br atom. As photon energy is varied, the two caging mechanisms display different dependence and lead to predictions of caging fraction that can be tested by experiment.

We also discuss refinements of our potential model for $Br_2^-Ar_n$: improvements of the Br-Ar potentials, relaxation of the point charge/point dipole model and, most importantly, a correct treatment of the dissociation limit $Br_2^- \rightarrow Br + Br^-$.

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6G

Metastable H_3^+ Formation and Decay in the Reaction of Highly Excited H_2^+ with H_2

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This paper presents the detailed results of a quasiclassical trajectory surface hopping study of reaction of highly vibrationally excited H_2^+ with ground state H_2 (and isotropic counterparts $H_2^+ + D_2$, $D_2^+ + H_2$ and $D_2^+ + D_2$), with particular emphasis on the formation and decay of metastable H_3^+ products. A diatomics-in-molecules surface is used which has been successful in previous studies of $H_2^+(v) + H_2$ at low v. In the present study, we consider v = 0–17, and find that metastable H_3^+'s are a major product for $v \geq 13$. Some of these metastables decay rapidly, showing exponential lifetime distributions with 2–7 ps lifetimes depending on v and on isotope. The remaining H_3^+'s have much longer lifetimes, and a number of methods are used to determine the origin of their stability. In no cases are any of these molecules found to be quasiperiodic, but a Fourier spectral analysis does reveal partial decoupling of H^+–H_2 orbital motion from H_2 rotational motion, such that orbital motion centrifugal barriers prevent dissociation. The variation of these centrifugal barriers with isotope and angular momentum is used to explain dissociation branching ratios for a number of processes. The relation of these results to recent infrared absorption measurements on highly excited H_3^+'s is discussed.

6H

Vibrational Energy Transfer in Collisions of Rare Gases with Highly Excited CS_2

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Recent work by Dove Hippler and Troe[1] has provided values for the average vibrational energy transfer $<\Delta E_V>$ in collisions of highly excited CS_2 with rare gas atoms and small molecules. These $<\Delta E_V>$'s vary strongly with the initial internal energy E_{int} and with collision partner. In this paper, the results of a classical trajectory study which is designed to simulate these experiments are presented. In this study we have used a spectroscopically derived potential for CS_2 and a sum of van der Waals' pair potentials for the intermolecular potential. We have calculated vibrational, rotational and internal energy transfer moments as a function of CS_2 internal energy, bath gas temperature and rotational angular momentum for several rare gases. We find that $<\Delta E_V>$ is quite sensitive to the assumed rotational energy distribution, with values that bracket the experimental results as the distribution varies from thermal (cold) to microcanonical (hot). This can be attributed to the changing role of rotation in influencing transfer pathways. Possible models for describing internal and rotational energy distributions present in the experiments will be discussed.

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7A

Monte Carlo Path Integration in Real Time via Complex Coordinates

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A Monte Carlo path integration method for calculating matrix elements of complex-time propagators, $\langle x| \exp\{-(\beta/2 + it/\hbar)H |x'\rangle$, which is also valid at long times ($t >> \hbar\beta/2$) will be presented. The essential new feature is a distortion of the integration path into the complex plane, thereby significantly postponing the onset of wild oscillations common in Monte Carlo evaluations of multi-dimensional integrals with oscillatory integrands. This Feynman path integral approach is an alternative to basis set methods and shows the greatest promise for handling the dynamics of many-mode "system - (harmonic) bath" problems.

A Theoretical Study of the Rate Constant for the Addition of Atomic Hydrogen and Muonium to Acetylene

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The thermal addition of hydrogen atoms to acetylene in the presence of a buffer gas M,

$$H + C_2H_2 + M \rightarrow C_2H_3 + M$$

has long been a puzzle in as much as many measurements of the rate constant in the high pressure limit produce A factors which are much lower than those for the corresponding addition in ethylene and which are inconsistent with TST and RRKM analyses of the reaction [see Harding, et al., *J. Phys. Chem.* **86**, 4312(1982)]. One potential explanation is that the hydrogen atom measurements have reached a false high pressure limit.

The recent implementation of improved theoretical techniques has prompted a new analysis of this system. Further, experiments studying the addition of muonium (Mu) to acetylene provide an additional source of rate constant data for this system. Muonium is like a hydrogen atom but with a positive muon substituted for the proton. Using a particle accelerator to create positive muons, muonium atoms with aligned nuclear spins can be produced. The rate of spin relaxation due to complex formation with any reactive species can then be measured. Such experiments are currently being conducted at TRIUMF.

Both the measured rate constants and RRKM and TST analyses of these reactions using the *ab initio* potential energy surface reported in the article cited above will be presented. While it has not been possible to fit simultaneously the experimental measurements of the high-pressure rate constant for the addition of both atomic hydrogen and muonium to acetylene, the current work does find better agreement between the experimental measurements and the theoretical calculation of the high-pressure hydrogen addition rate constant than was observed in the earlier study. As expected, tunneling plays a significant role in the calculation of the rate constant for muonium addition to acetylene. The calculations also suggest that muonium addition reactions, in contrast with abstraction reactions, characteristcally will have minor variational effects.

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7C

MULTIDIMENSIONAL VIBRATIONAL EIGENSTATES FROM A SEMICLASSICAL DYNAMICAL BASIS SET

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We present a new method for obtaining fully quantum mechanical eigenstates using an efficient basis set made up of semiclassical eigenstates. This basis is constructed from a primitive basis set of Gaussian wave packets placed uniformly on a phase space manifold defined by a single classical trajectory (an N-torus). (An accurate Fourier analysis of the classical dynamics is used to parametrize the N-torus numerically in the action-angle variables, then the "primitive" Gaussians are distributed on the manifold at uniform grid positions in the angle variables.) The "primitive" Gaussians are contracted to form semiclassical eigenstates by Fourier transform in a manner analogous to the spectral quantization procedure of DeLeon and Heller.[1] Since these semiclassical eigenstates are an extremely good approximation to the true quantum eigenstates, small matrix diagonalizations are sufficient to obtain quantum eigenvalues converged to 4-5 decimal places. Such diagonalizations need not include the ground vibrational state and thus do not rely on the variational principle for convergence. Results for several multidimensional model Hamiltonians are presented.

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7D

Direct Numerical Solution of Master Equation Transport on Disordered Lattices and Polymers

by
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An efficient numerical Green's function approach based on the Lanczos algorithm and the recursive residue generation method is used to study systems in which the dynamics can be approximated by the Pauli master equation. Applications include the calculation of transport observables on two-dimensional, classical percolating networks and the modeling of exciton transport on polymers. For the percolation problem, the mean-square displacement, diffusion coefficient, and probability of returning to the origin and the survival probability on systems with traps are presented for clusters of up to 440,000 sites. Using these results, accurate dynamical critical exponents are extracted, and the time and density regimes over which scaling theory is quantitative are delineated. In addition, the fluctuations in the random walk as a function of time and density are exhibited.

We have also studied transport in polymeric systems in an effort to characterize polymer morphology and dynamics under various conditions. Monte Carlo ensembles of self-avoiding random walks consistent with a given temperature, trap density and attractive energy between unbonded but adjacent chromophores are generated; the survival probability is then calculated for each configuration using our method. By systematically varying the model parameters, the dependence of the experimentally observable fluorescent intensities (directly related to the survival probability) on the polymer structure is mapped out, thereby facilitating the interpretation of time-resolved spectroscopic measurements on polymers in terms of their morphology.

7E

Stretch-Bend Coupling and Intramolecular Energy Transfer from Overtone Excited C-H Bonds: Benzene and CF_3H [a]

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Stretch-bend coupling via a 2:1 Fermi resonance has been proposed as an important mechanism for subpicosecond initial energy flow out of overtone excited C-H bonds in molecules such as benzene and CF_3H. In addition to the kinetic coupling between bend and stretch motions that results from the bond length dependence of the effective bending mass, potential coupling is also likely to be important, reflecting attenuation of the bending force constant with bond extension. Recent trajectory studies on overtone relaxation in planar benzene indicate that the decay rate is quite sensitive to the magnitude of the potential coupling [1]. To elucidate the role of potential coupling, we have studied the dynamics of a 2-mode model system representing a C_3H fragment of benzene, for which the magnitude of the potential coupling can be varied. The short time (up to 0.25 ps) CH energy relaxation behavior in the 2-mode model is in excellent qualitative accord with the full trajectory simulations of Lu et al. [1], and reasonable values for relaxation rates are obtained in the cases where exponential decay is observed. Surfaces of section reveal an intrinsically 2:1 resonant phase space, and point up the inadequacy of "pendulum" Hamiltonians to model the dynamics. The key to understanding relaxation in the model is the stability of the fixed point corresponding to the CH stretch [2]. If this fixed point is stable, overtone relaxation does not occur; conversely, instability is required for exponential decay. Increasing the magnitude of the potential coupling decreases the range of instability of the fixed point, and thereby suppresses overtone relaxation. Linearization around the fixed point leads to remarkably good estimates for relaxation rates [2]. We also report on similar studies of stretch-bend interactions in CF_3H, using the so-called "universal" effective Hamiltonian.

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c) Alfred P. Sloan Foundation Fellow.

7F

Classical Trajectory Studies of Overtone Induced Dissociation of HOOH, HOOD and HONO[a)]

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We present a classical trajectory study of the dissociation of HOOH, HOOD, and HONO induced by OH overtone excitation (v = 6, 7, 8). Simple near-separable model potential surfaces are employed, in which local bond stretches are described by Morse potentials, bending potentials are taken to be harmonic with force constants attenuated in BEBO fashion by stretching of the central bond, and the torsional potential is written as a Fourier series. Approximate curvilinear mode energies are followed as a function of time for 1 ps after OH bond excitation. The influence of rotations is investigated by studying three cases: a) Rotationless molecules; b) A thermal rotational distribution corresponding to T = 300 K; c) Rotation around the z-axis (perpendicular to the molecular plane). In all cases, energy flow from the initially excited OH stretch mode into the reaction coordinate proceeds via the neighboring bending mode. The lack of complete vibrational energy randomization together with a nonstatistical energy distribution in the fragments is indicative of non-RRKM behavior in the overtone induced dissociation. For HOOH, v = 6, rotation does not have a large effect on the dissociation rate; rotation around the z-axis slightly inhibits fragmentation, while thermal rotational excitation results in a slight increase in reaction rate. Lifetimes are in all cases close to statistical estimates. For HOOH, v = 7, dissociation lifetimes in the absence of rotation are extremely long; rotational excitation has a dramatic effect on the lifetime distribution. Results for HOOD and HONO are also presented.

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76

A Semiempirical Method for Determining HyperRaman Scattering Intensities

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Recent advances in surface spectroscopy have enabled the straightforward measurement of hyperRaman spectra for a variety of adsorbates on certain metal surfaces. For many molecules, it is not possible to measure the corresponding bulk hyperRaman spectra, and because of this, the surface contribution to these spectra cannot be determined. One way to circumvent this problem is to evaluate the bulk intensities via molecular orbital methods, but since many of the molecules are quite large, standard ab initio approaches are prohibitive. In this paper we present a semiempirical method for evaluating hyperRaman intensities, as well as related spectral information such as Raman intensities, polarizabilities and hyperpolarizabilities. The method has thus far been formulated using PPP wavefunctions, and in this case the evaluation of intermediate state sums is done directly, using singly excited configuration interaction calculations. Applications to pyridine will be discussed.

7H

Classical Trajectory Study of the Dynamics of the Reaction of $O(^1D) + H_2 \rightarrow OH + H$: The Mechanism of Formation of Vibrationally Excited OH

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A considerable proportion of the nascent OH ressulting from the reaction of $O(^1D) + H_2 \rightarrow OH + H_2$ is vibrationally excited, (v = 1-4). Experiments indicate that the distributions are not statistical but rather flat and perhaps inverted. It is tempting to assume that two reaction mechanisms are involved: an insertion mechanism which results in vibrationally cold, rotationally hot OH distributions and an abstraction mechanism that produces vibrationally excited OH. Recent experimental[1] and theoretical[2] results, however, suggest that the majority of vibrationally excited OH is produced via an insertion/elimination mechanism.

In order to further our understanding of the production of vibrationally excited products in reactions involving potentials with deep wells, we have studied classical trajectories on two realistic potential surfaces[3], SL1 and SL3, using a variety of techniques to generate initial conditions and analyze the trajectories. We present the results of this investigation. These studies include an exploration of the effects of H_2 rotation on the OH product state distributions. We also present theoretical OH rotational state distributions for OH in v = 1,2,3 and compare with recent experimental results obtained in our laboratory.[1]

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3A

DYNAMICS OF $H+O_2$ COLLISION ON THE AB INITIO POTENTIAL ENERGY SURFACE

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The dynamics of elementary rate process for $H+O_2$ Collision on the ab initio potential energy surface has been simulated by quasiclassical trajectory theory (QCT). For $H+O_2$ (v=o, j=1), we have obtained the reaction probabilities Pr(E , b) as function of collision energy E and impact parameter b, the reaction cross section σ_R as function of E, the average values $\overline{V}'_\alpha$, $\overline{j}'_\alpha$ of product state ($\alpha=O_2$, OH), they are both increasing as E goes up, at fixed E , $\overline{V}'_{O_2}$ decreases with b increasing, $\overline{j}'_{O_2}$ goes to maximum as b is about 3.0 a_0 in lower E (0.6-2.4 ev) and 2.5 a_0 in higher E (2.4-4.2 ev).

For $H+O_2$ (v=2, j=1, 20, 40, 60, 80, 100; v=1, 3, 4, 5, j=1), at E =0.3ev, we have found: b_{max} is about 4.5 a_0 and b_{pmax} at which Pr is maximum decreases as j increases; σ_R monotonically increase as j and V beacome large; for inelastic collision, when b is small and j is large, the $\overline{V}'_{O_2}$, $\overline{j}'_{O_2}$ both fall down; for reactive collisions, $\overline{V}'_{OH}$ almost equals to zero, but the probabilities of $\overline{V}'_{OH}$ being larger than zero obviously increase with increasing j; and the population inversion of $\overline{V}'_{OH}$ appears at j=100.

In addition, some figures of R_{ij}-t (Karplus) and stereograph (by us) have been plotted. From the latter one the collision mechanism can be easily visualized in more detail. According to those plots, the angular distributions of products and the durations of collisions which are usually long (the longest one of them being more than 1000 mtus) it is clearly seen that the collision process of $H+O_2$ seems to be very complex.

Acknowledgement: We thank Professor J.M.Bowmen for providing program.

AD-A195 528 AMERICAN CONFERENCE ON THEORETICAL CHEMISTRY HELD IN GULL LAKE MINNESOTA ON JULY 25-31 1987(U) MINNESOTA UNIV MINNEAPOLIS D G TRUHLER 1988 AFOSR-TR-88-0428 2/4

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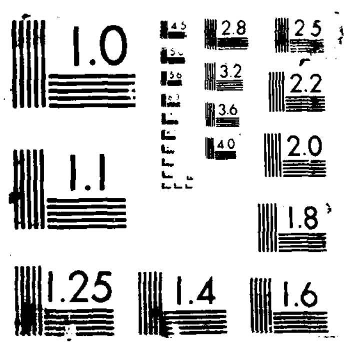
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8B

GENERALIZED WAVE PACKET DYNAMICS

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We extend wave packet dynamics to include complex positions and momenta using real time. Thereby we obtain a semiclassical method that is able to :

a) give time dependent wave functions that may show quantum features as e.g. interference. Only that part of the wave function which is needed is calculated, thereby avoiding unnecessary work. E.g. application to the autocorrelation $< \Psi(0) \mid \Psi(t) >$, where $|\Psi(0)>$ is a well localized initial state, results in a economic way to compute spectra.

b) describe classically forbidden processes. There is no semiclassical method known that is able to treat multidmensional tunneling. Miller's method of complex time works well for one dimension but encounters difficulties in higher dimensions because there is too little control over the trajectory. In contrast, using complex position and momentum, the number of parameter with which to control the trajectory increases with dimension. We therefore expect to be able to describe multidimensional tunneling.

We describe the dynamics of a system by matrix elements of the time propagator. The following matrix elements are calculated: $<g: a_1,q_1,p_1 \mid \exp[-iHt] \mid g: a_2,q_2,p_2>$ where $|g>$ is a gaussian wave packet $<x|g>= \exp[-a(x-q)^2+ip(x-q)]$, including position and momentum states as limits. The method assigns to every real position and momentum pair $(q,p)_r$ a continuous set of complex $(q,p)_c$. A path in complex phase space is searched that starts in the initial set and ends after a given time in the final set. By propagating a wave packet along this path an approximation to the above matrix element is obtained. Choosing the final gaussian to be narrow in position we may obtain directly a position space representation of the wave function.

CANCELLED

8C

TIME DEPENDENT THEORY OF GAS-SURFACE ENERGY TRANSFER

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Several time dependent studies have been made of gas-surface scattering in recent years, using both discrete[2,3c,4] and Gaussian wave packet[1,3a,3b] representations of the molecular wave function. All attempts to introduce finite surface temperature have involved a classical propagation of the surface atoms[2,3a], which is invalid for gas species of low mass or energy. We present a fully quantum mechanical theory of gas-surface energy transfer, which can be easily applied to any of these time dependent approaches. Using perturbation theory, the reduced density matrix for the gas atom/molecule is written in terms of three wave function-like objects, which obey Schrödinger-like equations of motion. Thus, the time evolution of the reduced density matrix requires only about three times the computational effort of the zero temperature calculation. The theory allows one to compute thermally averaged properties of the scattering molecular system at all times.

Results are presented for the scattering of He and Ne from various metal surfaces. The influence of coupling to bulk phonons and Raleigh modes is examined. Extensions to time dependent studies of dissociative adsorption[3c] and rotationally inelastic diffraction[3b,4] are considered.

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8 D

TIME-DOMAIN CALCULATION OF OPTICAL SPECTRA OF MULTIMODE SYSTEMS

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Calculation of optical spectra for systems with a large number of vibrational degrees of freedom requires casting the normal energy frame expressions for the intensity in the time domain. The resulting time correlation functions consist of a product of exponential operators containing vibrational Hamiltonians for the surfaces connected by the spectroscopic transition.

Calculation of these real time kernels without making drastic assumptions about the nature of the potentiial energy surfaces involved poses a challenging problem for theorists.

In this paper we present analytical and numerical development of a computational scheme for computing the exact time correlation functions for absorption, fluorescence, and resonance Raman scattering for general harmonic potentials.

The method allows inclusion of linear and quadratic Franck-Condon interactions as well as linear non-Condon effects, and is based on an algorithm for combining products of exponential harmonic operators into a single exponential operator with a harmonic Hamiltonian. Calculation of the thermal average is carried out using standard many-body phonon techniques. Frequency spectra are produced via numerical Fourier transform.

We apply this technique to the simulation of absorption and resonance Raman spectra of systems which would be difficult if not impossible to treat with alternative methods.

8E

TIME-DEPENDENT ANALYSIS OF THE HARTLEY ABSORPTION BAND AND RESONANCE RAMAN SPECTRA IN OZONE

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Abstract

A detailed investigation is made of the *short-time dynamics involved in the* Hartley absorption band in ozone and the related resonance Raman spectra for low vibrational overtones. A quadratic expansion of the X^1A_1 and dissociative $^1B_2$ potential energy surfaces involved leads to an analytic calculation of three-mode vibrational correlation functions, which are then Fourier-transformed to obtain the absorption and Raman spectra. A type of time-dependent perturbation theory is used to approximate the effects of including anharmonic terms in the expansion of the upper state. It is concluded that an improvement in the description of the Raman spectra will require at the least a major modification of the parabolic barrier behavior along the antisymmetric stretch coordinate and, better, a large-amplitude-motion treatment.

8F

Time Dependent Hartree Fock Theory of $H^+ + H_2$ Reactive Scattering*

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Using a fully self consistent, time dependent Hartree Fock method[1], the collinear reactive scattering of a proton by a hydrogen molecule has been studied for a number of collision energies (< 3eV) and initial vibrational levels. In these calculations, the electronic state corresponding to charge transfer with or without reaction is included. The nuclear motion is treated classically, with a potential calculated using the instantaneous electron density distribution. The electron density, represented by a single Slater determinental wave function, defined on a finite difference grid, evolves in the field of the moving nuclei. These calculations incorporate non-adiabatic effects due to the nuclear motion and some degree of dynamic correlation in the electronic wave function.

A separate calculation is carried out for each collision energy and vibrational level with a particular initial phase of the vibration. An average over the phase has been carried out. Results include averaged charge transfer probabilities and the degree of vibrational excitation in the products. In all cases considered, the trajectories were found to be reactive. Time dependent density contours for the electrons and trajectories of the nuclei provide information about the dynamics of the reaction process.

Details of the calculations and the results will be presented. Conclusions about the velocity dependence and vibrational state dependence of the charge transfer and reaction probabilities are consistent with the surface hopping results of Tully and Preston[2] and the quantum mechanical results of Top and Bear[3].

*This work was performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.

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86

CLASSICAL TRAJECTORY CALCULATION OF THE BENZENE OVERTONE SPECTRA

Da-hong Lu and William L. Hase

In previous research,[1] it was found that intramolecular vibrational energy redistribution (IVR) from benzene overtone states is very sensitive to potential energy coupling between the excited CH(D) stretch and the contiguous CCH(D) bending motion. Using a potential energy function which includes an expression for this coupling derived from ab initio calculations,[2] IVR from benzene overtone states is studied with the quasiclassical trajectory method. The probability, P(n,t), of populating the initially prepared overtone state $|n\rangle$ is calculated for benzene CH and CD overtone states. Absorption envelopes are determined from the Fourier transform of this probability. The resulting absorption linewidths are in excellent agreement with those reported by Reddy et. al.[3] The decreases and increases in the linewidths versus $|n\rangle$, observed experimentally, are also found in the trajectory study.

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8H

Calculation of Reaction Rates for a System Coupled to a Harmonic Bath: Basis Set Methods and the Time-Dependent Self-Consistent Field Approximation

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Quantum mechanical basis set methods have been developed for calculating reaction rates for a model consisting of a "system" (e.g., a one-dimensional reaction coordinate) coupled to a "bath" of many harmonic oscillators. By choosing the basis set for the bath to incorporate the coupling explicitly, it is shown how the bath can then be eliminated to obtain an effective Hamiltonian matrix for only the system. Numerical calculations have been carried out which show that, even in the zeroth order version of the approach, the effect on the system (e.g., the tunneling splitting in a symmetric double well potential) of coupling to the bath is described well, even when the effect is extremely large.

Time-dependent methods for following the dynamical evolution of the system are also considered. The time-dependent self-consistent field approximation is tested for the system-bath model in the cases of symmetric and asymmetric double well potentials, and the results are compared to those obtained by the basis set methods.

9A

Abstract for the
1987 American Conference on Theoretical Chemistry

COLLISIONAL ENERGY TRANSFER INTO MOLECULAR ADSORBATES: A TIME-CORRELATION FUNCTION APPROACH*

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Double differential cross sections for the energy and angular distributions of He and Li^+ scattered by CO adsorbed on the Ni(001) surface have been obtained from collisional time-correlation functions. Results have been derived in the limit of impulsive collisions and within a statistical model that accounts for single and double collisions. These lead to clearly separate energy and angular distributions of products.[1,2]

1. David A. Micha, Int. J. Quantum Chem. Symp. 19, 443 (1986).
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* Work partly supported by the National Science Foundation.

9B

The Aggregation of Oriented Anisotropic Particles

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The formation of cluster by the aggregation of small objects and by growth processes is a subject of considerable interest and of practical importance in physics, chemistry, biology, medicine, and engineering. In practice there are a lot of aggregation phenomena such as particles with induced dipole moments in an external field, magnetic particles in an external field and polymerization in an ordered liquid crystal. Aggregation in ferrofluid is a particularly interesting example with condiderable scientific and practical importance.

In this paper the limited aggregation of oriented anisotropic particles is investigated using computer simulations. Figure 1 below shows patterns formed linear rods in the 512× 512 square lattice. Initially 8000 particles are distributed and the average cluster size is 20.19 and diffusion constant is assumed to be proportional to s^{-1}. Figures 2(a) and 2(b) blow show patterns formed linear rods in 3-dimensional cubic lattice (128^3), where 10,000 partcles and distributed initially and average cluster size is 40. Figures 2(top two) are intersected by a plane including the external field and Figs. 2 bottom right and left are a projection onto and an intersection by a plane respectively that is perpendicular to the external field. The aggregation process is well described by the cluster-size distribution function $N_s(t)$, which is the number of clusters of size s at time t.

By the dynamicl scaling theory the time dependent cluster-size distribution can be represented by the scaling form $N_s(t) = s^{-2}f(s/S(t))$ where $S(t)$ is the mean cluster size. At high particle densities a crossover from two (or three) dimensional behavior to that that is characteristic of a one dimensional system is found.

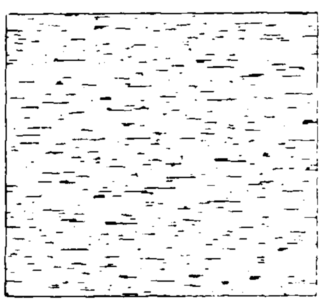

Fig. 1

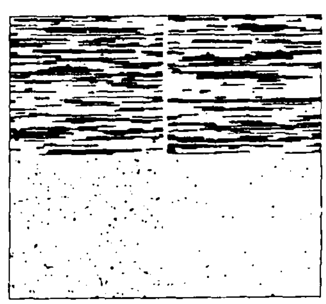

Fig. 2

9C

Fluorescence, Raman and Four-Wave Mixing Spectroscopy in Polar Solvents

- A Probe for Vibrational and Solvation Dynamics

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A microscopic unified theory is developed for time-domain and frequency-domain four-wave mixing and spontaneous Raman and fluorescence spectroscopy of polyatomic molecules in condensed phases. Both experimental observables are expressed in terms of the four-point correlation function of the dipole operator which may be evaluated microscopically. The present formalism is based on the equations of motion of the density matrix in Liouville space. It enables us to treat the relevant molecular vibrational degrees of freedom quantum mechanically, and perform a partial averaging over the solvent. Green function techniques are developed and used to eliminate the summations over the vibronic manifolds required in the calculation of nonlinear susceptibilities in harmonic polyatomic molecules.

The time and frequency resolved fluorescence spectrum of a polar molecule in a polar solvent is expressed in terms of gas phase spectroscopic parameters of the solute, vibrational relaxation rates, the dielectric properties of the solvent, and the temporal profile of the excitation pulse. The fluorescence spectrum is narrow at short times, and displays line broadening and a red shift as the solvent relaxes about the excited solute.

Effects of intramolecular and intermolecular vibrational redistribution on fluorescence lineshapes are analyzed. Other applications are made to coherent anti-Stokes Raman (CARS) and to the spectroscopy of ultracold molecules in supersonic beams (intramolecular solvation).

9D

Mean Relaxation Time Description of Quasi-Dissipative Behavior in Finite-State Quantum Systems

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ABSTRACT

The exponential decay of an initially prepared state coupled to a continuum of states is a well-known effect, the decay constant Γ being given by Fermi's golden rule. Even in quantum systems with only a finite number of states an approximately exponential decay of an initially prepared state can often be observed, the time scale τ of the decay being much shorter than the recurrence time T of the system. In order to determine the decay constant Γ in such a situation from the given Hamiltonian, we describe the probability amplitude for an initially prepared state observed experimentally on a time-scale γ^{-1} by a *mean relaxation time approximation* (MRTA).[1] The resulting decay constant $\Gamma(\gamma)$ is independent of γ for $\tau < \gamma^{-1} < T$, and its value in this regime constitutes the actually observed decay constant. We discuss the application of this method and its extensions to intramolecular energy-redistribution problems, and address also its limitations.[2]

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[2] W. Nadler and R. A. Marcus, manuscript in preparation.

9E

TIME-DEPENDENT DYNAMICS OF ELECTRONS AND NUCLEI IN MOLECULAR SYSTEMS.

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A new approach to molecular dynamics involving both electrons and nuclei is formulated from the Time-Dependent Variational Principle[1]. Averaging the fast dynamics of the electrons over a time τ effectively eliminates the fast fluctuations and brings the integration of the dynamical equations to the time scale appropriate for the physically interesting nuclear variables. When the pace of the dynamics speeds up, the averaging time is reduced so that no vital information is lost.

Applications to a simple model for electron transfer reactions are discussed and directions for future applications are given using a generalized wave packet dynamics for electrons and nuclei, which can employ a coherent state formulation[2].

References.

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9F

ABSTRACT

A NEW CRITERION FOR CONVERGENCE OF EXPONENTIAL PERTURBATION THEORY IN THE SCHRODINGER REPRESENTATION

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It is shown that exponential perturbation theory (which includes the Magnus expansion and Magnus-like expansions) in the Schrödinger representation does not converge for time intervals larger than a natural period of the system for several model systems of physical interest. This condition is related to that for harmonically driven systems in which the driving frequency must exceed the natural frequency in order for exponential perturbation theory to converge. This has unfortunate implications for the application of these theories in the Schrödinger representation to a number of important problems.

96

Rotational Decoupling:
Decoupling of Local Stretching Modes by Rotational Excitation
Model Studies of 2-dimensional H_2O and 3-dimensional O_3

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The intramolecular dynamics of highly excited molecules is of interest in spectroscopy, unimolecular reactions, infrared multiple photon absorption experiments, combustion, propulsion, and many other processes. Many theoretical studies have shown that vibrational energy is randomized or at least shared among vibrational modes of a molecule on the picosecond time scale. Recent experiments have observed rotational effects in the experimental measurements of fluorescence depolarization, stimulated emission pumping, laser induced fluorescence, etc. Unfortunately, almost all theoretical studies of intramolecular dynamics have neglected rotational motion.

It is commonly assumed that the additional coupling provided by rovibrational terms in the molecular Hamiltonian will increase the rate of energy flow, lower the threshold for the onset of the quasicontinuum, and increase the extent of classically chaotic motion. In model calculations, we <u>have</u> observed just these effects. However, it is also possible for rotational excitation to <u>decrease</u> the amount of vibrational energy flow. A model of the stretching motions of H_2O served as an initial example of this phenomenon which we named <u>rotational decoupling</u>.[1,2,3,4]

Rotational decoupling occurs when the terms describing kinetic coupling and potential coupling between vibrational modes are cancelled by terms describing centrifugal coupling. In this poster, we will review rotational decoupling in the initial classical and quantum studies of the H_2O model system (real three dimensional water does not show this effect because of the way the bend angle was fixed), and new results on the ozone molecule. We now believe that rotational decoupling will be seen in symmetric triatomic molecules in which the symmetric stretch frequency is higher than the asymmetric stretch frequency. The possible significance of rotational decoupling will also be discussed.

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9H

Theoretical Studies of Vibrationally and Rotationally Excited Polyatomic Molecules using Almost Degenerate Perturbation Theory

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The highly excited vibrational and rovibrational dynamics of polyatomic molecules are investigated using Almost Degenerate Perturbation Theory. The canonical form of Van Vleck perturbation theory is implemented in a superoperator formalism. This approach is used to transform the rovibrational Hamiltonian to a new representation which has a form ideally suited to the study of the dynamics of interest. The key advantage is that the solution to the full problem is obtained in the new representation using significantly smaller basis sets than are needed to obtain the solutions in the original representation. The transformations are applied to the Hamiltonian operator itself not the Hamiltonian matrix; this superoperator approach obviates the need for large basis sets. The tedious and complex algebra, that is required to perform these transformations, is readily implemented with FORTRAN codes. Combining these two features has enabled the investigations of vibrational and rovibrational dynamics in energy regimes and densities of states, unattainable by standard variational methods. These methods are applied to the study CH overtone dynamics of CHD_3 and rotation-induced vibrational mixing in formaldehyde on the ground electronic surface with $7400<E_{vib},8600$ cm^{-1}.

10A

Time-Dependent Photodissociation of Ozone

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The photodissociation of ozone in the Hartley band is studied theoretically by numerical integration of the time-dependent Schrodinger equation on a grid. Calculations reveal the coupled dynamics in the symmetric vs. asymmetric stretch and the asymmetric stretch vs. bend; the latter two coordinates reveal the full three-fold permutational symmetry of the molecule. Autocorrelation functions, cross-correlation functions, and projections of the moving wavepacket onto asymptotic states ($O_2\,{}^1\Delta_g$ + O ^1D) are calculated, and used to construct absorption spectra, resonance Raman spectra and vibrational and rotational final product distributions.

Energy Redistribution in and Dissociation of Molecular Clusters

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Recently, Lineberger and coworkers[1] have carried out experiments involving the $Br_2^-(CO_2)_n$ negative ion cluster. The Br_2^- ion is photoexcited to a repulsive electronic state which, in isolation, would dissociate to a Br atom and a bromide ion. In the cluster environment, however, the Br and Br^- may recombine with the accompanying loss or "evaporation" of one or more CO_2 molecules. The observed size distribution of the product ion clusters reflects the dynamics of energy transfer within the ion cluster. Due to the complexity of the $Br_2^-(CO_2)_n$ system, we have sought to understand this process through studies of simpler model systems.

Previous work in our group[2] has examined energy redistribution within the ion pair cluster $NO_2^-:Li^+(H_2O)_n$, n = 1,5, given a large initial relative velocity between the NO_2^- and Li^+ in an otherwise cold cluster. For this system, the internal vibrational level spacings are large enough that these modes could be safely ignored at the energies of our study. In the $Br_2^-(CO_2)_n$ experiments, however, the bend mode of the CO_2 molecules is energetically accessible, and the Br_2^- is, of course, formed in an excited vibrational state. We will describe work concerning the role of internal vibrational modes in the dynamics of these systems. An approximate quantum mechanical treatment of the internal vibrations, suitable for inclusion in a classical trajectory code, is being investigated, and further trajectory studies are planned.

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10C

Abstract for the 1987 American Conference on Theoretical Chemistry, Gull Lake, Minnesota, 27–31 July 1987

APPROXIMATE INTRAMOLECULAR DYNAMICS CALCULATIONS: ADIABATICALLY REDUCED COUPLED EQUATIONS

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ABSTRACT

The adiabatically reduced coupled equations approach to intramolecular dynamics calculations [J. Chem. Phys. **84**, 2254 (1986); **85**, 5019 (1986)] is extended to treat quasi-dissipative intramolecular dynamics and applied to some model molecular systems.

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10D

Time Delay in a Chaotic Quantum Scattering System

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The quantum treatment of a two degree of freedom scattering system originally studied by Gutzwiller† is re-examined and new results for the time delay obtained. Although apparently not corresponding to any known physical system, this system is exceptional in that its scattering can be solved analytically yet its behaviour, as indicated by the role of the Riemann zeta function, is inherently chaotic. It is hoped that this simple, albeit somewhat abstract, system will provide insights into the nature and manifestations of quantum chaos in the scattering regime. In order to make the model more intuitive, we have re-cast the mathematical treatment, dropped Gutzwiller's curved space interpretation, and have explained the meaning of the phase shift and time delay in terms of plane waves and wave packets.

Plots of phase shifts (which are identical to Gutzwiller's) and time delays as a function of the "velocity" are presented. The chaos in the phase shift is evident. The chaotic contribution to the time delay fluctuates smoothly between positive and negative values, displaying fairly sharp positive peaks reminiscent of resonances in conventional scattering systems. At the time of writing an analysis of these "resonances" was underway; some results of this analysis will be included in the poster.

†M.C. Gutzwiller, Physica 7D, 341 (1985).

10E

LASER INDUCED THERMAL DESORPTION: A THEORETICAL STUDY

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ABSTRACT

The dynamics of atomic adsorbate desorption following a fast laser induced surface heating is simulated. The simulations were performed using a stochastic trajectory approach where the adsorbate motion is described by an effective Langevin equation of motion. The thermal motion of the crystal atoms are incorporated by a correction term to the adsorbate-surface interaction potential, a friction term and a Gaussian random force. These therms are given in term of the solid parameters (i.e., mass, Debye temperature etc) as well as the adsorbate-surface interaction potential.
We have concentrated in this study on the simulation of the desorption of Xe from W(100) surface. Angular, translational energy and residence time distributions were calculated for different possible adsorption sites, potential energy corrugation, heating rates and coverages.
At the higher coverages, θ=0.8, adsorbate-adsorbate interactions were included. In general, the kinetic energy distributions of desorbates were found to be non Boltzmann with mean energies different than those corresponding to the surface temperature. Additionally, the angular distributions were found to significantly differ from a cos(θ) distribution. Finally, we found that all the distribution functions calculated strongly depend on initial coverage and the nature of adsorbate-adsorbate interactions.

Poster abstracts

Relativistic and spin-orbit effects in electronic structure

(alphabetical by name of presenter, which is underlined)

10F

ELECTRONIC STRUCTURE OF MOLECULES CONTAINING HEAVY ATOMS

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Relativistic effects such as mass-velocity correction, Darwin correction, and spin-orbit corrections are very important for molecules containing very heavy atoms. Electronic structure properties of molecules containing very heavy atoms are calculated using spin-averaged *relativistic effective core* potentials for the heavy atoms. The orbitals for Configuration Interaction calculations are generated using the CASSCF complete active space (MCSCF) method. Electron correlation is introduced through the MRSDCI technique. Spin-orbit interaction is then introduced in a variational relativistic CI (Configuration Interaction) scheme. We illustrate our procedure with a number of molecules containing heavy atoms such as Pt_2, Pd_2, PtH_2, PdH_2, PdH, RhH, Te_2, Au_3, etc.

106

RELATIVISTIC CALCULATIONS ON MOLECULES CONTAINING ATOMS OF THE TRANSURANIUM SERIES

by

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ABSTRACT

The only general methods available at the present time for performing relativistic electronic calculations on polyatomic molecules are of two types: 1. Those which use some local density functional expression for the exchange correlation term. 2. Those which use *ab initio* relativistic effective core potentials. Results obtained using both these approaches on compounds of the transuranium elements are presented.

Calculations using the Dirac Scattered Wave Xα (DSWXα) method have been performed on the tetrafluoride and tetrachloride of uranium. The results of these calculations are compared with the results of other calculations and, in the case of the ionization potentials, are compared with experiments. It is shown that the ionization potentials of these molecules can be used as a sensitive probe for investigating the nature of the ligand-metal interactions. This is in contrast to similar results on the corresponding octadecmal compounds which are relatively insensitive to these interactions.

In order to demonstrate the influence of relativistic effects on the bonding in molecules containing very heavy atoms relativistic and nonrelativistic DSWXα claculations on the hexacarbonyls of vanadium, niobium, tantalum and element 105 are presented.

One of the drawbacks of the DSWXα method is that the results are often sensitive to the atomic sphere radii used, i.e., to the amount of overlap between adjacent spheres. Also for compounds of the transuranium elements there are few experimental interatomic distances available. In order to compare the results of the DSWXα calculations with methods which do not suffer from the problem of the overlapping spheres, calculations on the hydrides, fluorides and chlorides of scandium, lutecium, lawrencium (element 103) and element 105 have been performed using the relativistic *ab initio* effective core potential method developed by Pitzer et al. The results of these calculations will be compared with DSWXα calculations performed at different sphere radii. DSWXα results using the optimized sphere radii on polyatomic fluoride and chlorides will also be presented.

ACKNOWLEDGEMENTS

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104

State Averaged MCSCF-CI Calculations on the Spin-Orbit Interactions of the Low Lying Triplet and Quintet Excited States of He2.

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Due to it's potential use as an energy storage medium, interest has been shown in the spin-orbit and collisional lifetimes of the low lying triplet and quintet excited states of He2. The relevant potential energy curves have been determined at the state-averaged MCSCF-CI level. The spin-orbit interactions were computed with the the recently introduced Symbolic Matrix Method for the spin-orbit Hamiltonian matrix elements (D.R. Yarkony, J. Chem. Phys., 84, 2075(1986)). In this method, the spin-orbit perturbations are computed in the CSF basis which alleviates the problem associated with other methods based on truncating a sum over states.

11A

Relativistic Effective Potentials in Lighter Element Calculations

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Applications of relativistic effective potentials involving molecules containing lighter elements (first and second transition rows, etc.) will be discussed. Topics will include core-valence correlation and partitioning, spin-orbit coupling, as well as recent quantum Monte Carlo studies.

113

Theoretical Study of the Intensity of the Spin- or Dipole-Forbidden Transitions $X^1\Sigma_g^+ - a^3\Pi_u$; $X^1\Sigma_g^+ - c^3\Sigma_u^+$ and $b^3\Sigma_g^- - c^3\Sigma_u^+$ in the C_2 Molecule

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The radiative lifetimes of the spin- or dipole-forbidden transitions $X^1\Sigma_g^+ - a^3\Pi_u$, $X^1\Sigma_g^+ - c^3\Sigma_u^+$ and $b^3\Sigma_g^- - c^3\Sigma_u^+$ have been determined by large-scale configuration interaction calculation employing a first order perturbation expansion and the transition mechanism has been analyzed.

The Hamiltonian used for the theoretical evaluation is:

$H = H_0 + H_{SO}$ whereby H_0 is the normal non-relativistic Hamiltonian including kinetic energy and electrostatic interactions and the term H_{SO} is the spin-orbit contribution taken from the Breit-Pauli formulation. The non-relativistic zero-order solutions are obtained in the standard multi-reference configuration interaction (MRD-CI) procedure for H_0. The H_{SO} effects are evaluated by a variational perturbation treatment in the basis of the zero-order solutions in which a matrix of the electrostatic and spin-orbit contributions is formed; all one- and two-particle effects are calculated. Upon diagonalization one obtains the perturbed energies and the corresponding wavefunctions which are then used for determining the forbidden radiative transitions.

INTERPRETING THE NMR 'HEAVY-ATOM CHEMICAL SHIFT'

11C

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Neighboring atoms to a heavy halogen X (Br,I) are known to show a large chemical shift which is upfield for main-group atoms (^{1}H, ^{13}C - ^{209}Pb), increases quadratically with the number of halogens, and increases with the s-character for sp^n hybridized ^{13}C. It has been explained[1] as a spin-orbit effect using 3rd-order PT: $\langle H_{hfs} \rangle \langle H_{Zeeman} \rangle \langle H_{so} \rangle / \Delta E \Delta E'$. Using relativistic (REX) MOs, and the relativistic analogue[2] of Ramsey's theory, 2nd-order PT is enough ($\langle H_{hfs} \rangle \langle H_{Zeeman} \rangle$). The shift is then attributed to so-induced spin-density in Zeeman-allowed but hyperfine-forbidden excitations, or vice versa[3]. Results are shown for ^{1}HX, $X^{13}C \equiv CH$, ..

HAHA. The *heavy nucleus* itself, when having lone pairs, shows an analogous shift. For ^{209}Pb in Ph_3Pb^-, $Pb_2Se_3{}^{2-}$ and $Pb(N(SiMe_3)_2)_2$, it is ca. +1050[4], +3290 and +4916 ppm (downfield from $PbMe_4$), respectively. REX calculations on a simple $PbH_3{}^-$ model suggest a major contribution from 6s hfs, a "heavy-atom shift of the heavy atom"[4].

1 Nomura, Y.; Takeuchi, Y.; Nakagawa, N. Tetrahedron Lett. **1969**, 639.
2 Pyykkö, P. Chem. Phys. **1983**, 74, 1.
3 Pyykkö, P.; Görling, A.; Rösch, N. Mol. Phys. **1987**, 00, 000.
4 Edlund, U.; Lejon, T.; Pyykkö, P.; Venkatachalam, T.K.; Buncel, E. J. Am. Chem. Soc. (submitted).

11D

Atomic Spin-Orbit Splitting Energies Calculated Using Relativistic Effective Core Potentials

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Spin-orbit splitting energies have been calculated for selected main group atoms from Z=5 through Z=86 employing ab initio spin-orbit operators based on relativistic effective potentials.[1] Extended basis sets comprised of both Slater- and Gaussian-type functions are used to describe valence electrons. A computer program is described that performs, in addition to spin-orbit coupling calculations, atomic self-consistent field calculations in L-S and j-j coupling. Spin-orbit splitting energies agree to within 8% of experiment in most cases. This is contrasted to those computed using Hartree-Fock wavefunctions and the full microscopic spin-orbit Hamiltonian, where errors as large as 34% result for atoms of the fifth row of the periodic table.[2]

[1] W.C. Ermler, Y.S. Lee, P.A. Christiansen, and K.S. Pitzer, Chem. Phys. Lett. **81**, 70 (1981).
[2] R.B. Ross, W.C. Ermler, and P.A. Christiansen, J. Chem. Phys., **84**, 3297 (1986).

Poster abstracts

Electronic structure of molecules, reactions, and solids

(alphabetical by name of presenter, which is underlined)

11E

MOLECULAR STRUCTURE CALCULATIONS FOR BORON HYDRIDES

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and

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ABSTRACT

As part of a larger project to predict thermochemical data for various classes of boron containing compounds, we have applied our quantum chemical methods to determine the structures of a number of boron hydride compounds. The unique topological features characteristic of the molecular structures of boron containing compounds are manifested in even the smallest of the boranes. Our presentation will focus on compounds containing two or three boron atoms.

The molecular structure calculations were performed using computer codes developed at the BRL and LANL during the past several years. Some calculations were run using GAUSSIAN82 to verify the results obtained with our codes. All the calculations used double zeta plus polarization function basis sets. First- and second-derivative based searching algorithms were used. The structures reported all correspond to stable points that possess all positive second derivatives.

We will report results for B_2H, B_2H_2, two isomers of B_2H_3, B_2H_4, and B_2H_5, and B_2H_6. The B_3 compounds include the classical and two nonclassical isomers of B_3H_5, two isomers of B_3H_7, and one structure for B_3H_9.

To the extent that results are available, we will also report results of correlation method calculations to predict the relative stability of the various isomers.

11F

CHEMICAL ACCURACY: METHODS AND RESULTS FOR POLYATOMIC SYSTEMS

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If chemical accuracy is defined to be 1 kcal/mole, most of the traditional methods associated with quantum chemistry (large CI and MCSCF calculations, as well as perturbation and coupled cluster calculations) can achieve this goal only with great computational effort. Pair functions are an accurate and efficient solution to this problem. These explicitly correlated two-electron functions are a generalization of molecular orbitals and when used in perturbation or coupled cluster calculations they show a much faster convergence than similar calculations with molecular orbitals. In this poster we shall describe a method of performing such calculations which we call random tempering because of its resemblance to even tempering. Results for both atomic and molecular systems will be presented.

11G

STUDY OF ACIDITY IN ZEOLITES MATERIAL (FAUJASITE) BY "AB INITIO" TYPE CALCULATIONS.

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Zéolites are porous substances commonly used in industry as molecular sieves to separate molecular species. They may also act as catalytic agents or acid medium.

The purpose of the present work is to study the proton donor capacity (acidity in the sense of Brönsted) of one type of zéolite (i.e. the Faujasite species).

The calculation are performed at the SCF level using mostly 6-31G basis set functions. Also pseudo potential method has been used and the data so obtained are compared to "ab initio" results.

The Faujasite bulk system is simulated by cluster built with the nearest neighbor atoms surrounding the acidic hydroxyl group. $Si(OH)_4$, SiOH AlH_6 and SiOH $Al(OH)_6$ clusters are considered. Partial optimization by gradient method is performed at the 6-31G level. Deprotonation energy and atomic charges are calculated using the same basis set as well as extended basis sets including polarization functions on all atoms or heavy atoms only.

Effect of replacing Al atom by B,Ge and Ga atoms are also investigated.

Study of the proton transfert has also been examined by comparing the stability of the two complexes : $ZOH..NH_3$ and $ZO^-...NH_4^+$, where ZOH represents the $SiOHAl(OH)_6$ cluster. The hydrogen bonded complex is the most stable.

Interactions with other molecular systems are under study.

Solvation effects are evaluated using some crude approximations.

11H

Analytic Configuration Interaction Energy First Derivatives for Open-Shell Singlet Excited Electronic States of the Same Symmetry as the Ground State. Application to the 2^1A_1 States of Formaldehyde and Ketene

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The efficient two-configuration self-consistent-field configuration interaction (TCSCF-CI) gradient method recently implemented by Lee, Allen, and Schaefer[1] is adapted and applied to open-shell singlet excited electronic states of the same symmetry as the ground state. The procedure makes use of the Z-vector approach of Handy and Schaefer[2] and does not require the transformation of derivative integrals. Since single-configuration self-consistent-field configuration interaction (SCF-CI) wave functions are unreliable for such electronic states due to the possibility of variational collapse, the TCSCF-CI method based on excited-state orbitals is the simplest means by which dynamical electron correlation can be incorporated effectively. Geometrical structures, excitation energies, and harmonic vibrational frequencies obtained with double zeta plus polarization (DZP) and DZP + Rydberg (DZP+R) basis sets are reported for the 2^1A_1 states of formaldehyde and ketene. The 2^1A_1 surface of H_2CO is predicted to have two distinct C_{2v} minima with T_0 values of 64000 cm^{-1} and 68100 cm^{-1} corresponding to $n \rightarrow 3p_y$ and $\pi \rightarrow \pi^*$ excitations, respectively. The 2^1A_1 state of CH_2CO is found to be Rydberg in character with T_0=56000 cm^{-1} and a geometrical structure very similar to that of the $^2B_1$ CH_2CO^+ ion.

---

[1] T.J. Lee, W.D. Allen, and H.F. Schaefer III, J. Chem. Phys., submitted for publication.

[2] N.C. Handy and H.F. Schaefer III, J. Chem. Phys. **81**, 5031 (1984).

12A

Quantum Chemistry by Random Walk:
Application to the Potential Energy Surface for $F + H_2 \rightarrow HF + H$

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We have applied the random walk method of solving the Schrödinger equation to determine energies of the following species: the fluorine atom F, the hydrogen fluoride molecule HF, and a number of F-H-H configurations of interest in determining the height and location of the saddle point for the reaction $F + H_2 \rightarrow HF + H$ and the characteristics of the potential energy surface in the region of the barrier [1]. Several of the F-H-H configurations examined correspond to those suggested as saddle points in "The Ecstasy and the Agony" [2] of past variational calculations.

In what may be "Paradise Regained" we obtain electronic energies for these species which are approximately 65 kcal/mol below those of the lowest-energy variational calculations and for F and HF are only about 9 kcal/mol above the relativity-adjusted experimental values. Recovery of correlation energy is 96 percent complete. Since there is little room left for error, differences in energies among $F \pm H_2$, F-H-H, and HF + H are expected to be relatively free of error. The calculated exothermicity of the reaction is 29.7 ± 1.5 kcal/mol, which may be compared with the experimental value of 31.7 ± 0.2 kcal/mol.

Thus far, we have obtained potential energies for F-H-H with statistical uncertainties of about 1 kcal/mol, but these can be reduced in further calculations. There has been much discussion and speculation on the height and location of the saddle point, linear and non-linear transition states, the effects of various terms included in CI calculations, the use of empirical corrections, the relationship between activation energy and barrier height, the zero-point energy of the 'transition state,' threshold energy for reaction, tunneling in the real 3-D system, and quantum resonances observed in crossed-beam experiments. None of these things can be completely understood without a potential energy surface of known high quality. We expect to reduce statistical error for the most important configurations so that the surface can be determined with sufficient accuracy to resolve many of these questions.

[1] D. R. Garmer and J. B. Anderson, J. Chem. Phys., submitted (1987).
[2] H. F. Schaefer, J. Phys. Chem. 89, 5336 (1985).

12B

THE STEREOCHEMISTRY OF DIELS-ALDER REACTIONS OF CYCLOPROPENES. EXPERIMENT AND THEORY.

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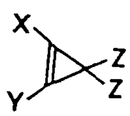
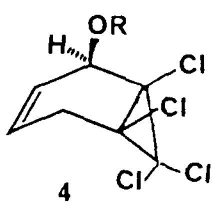
The Diels-Alder (DA) reaction was studied extensively in the last decades, both experimentally and theoretically. Suprisingly, the knowledge on the stereochemistry of DA reactions of cyclopropenes is confusing and the factors that control the stereoselectivity of these reactions are poorly understood. In this paper we report the first unequivocal data (based on X-ray analysis) on the stereochemistry of the DA reactions for 3 substituted cyclopropenes 1-3 with 1-methoxybutadiene and analyse these reactions on the basis of ab initio calculations for the endo (7) and exo (8) transition states (T.S.).

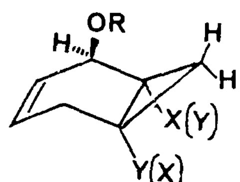
1 gives exculsively the exo adduct 4. This is attributed to the strong steric interactions in the endo T.S. between one of the gem-chlorines of 1 and the butadiene. In the exo T.S. steric interactions are much smaller. In contrast, with the parent 3 only the endo product 6 is observed. With 2, the stereoselectivity is lower but the endo product dominates, the product ratio being endo 5: exo = 9:1. As steric effects favor the exo T.S. the observed endo stereoselectivity is dictated by electronic effects.



1, X = Y = Z = Cl
2, X = Cl, Y = Br, Z = H
3, X = Y = Z = H

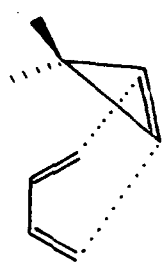


4

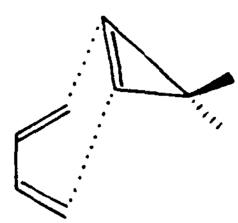


5, X = Cl, Y = Br
6, X = Y = H

The T.S. for the parent reaction, endo (7) and exo (8) were calculated by ab initio techniques. The computational results are in agreement with the above experiments: e.g., at 3-21G 7 is lower in energy than 8 by 2.4 kcal/mol. The factors which dictate the endo stereoselectivity in these DA reactions and the geometries of the isomeric T.S. will be discussed.



endo (7)



exo (8)

12C

Theoretical Studies of Three-Membered Rings X_2H_4Y (X=C,Si; Y=CH_2,NH,O,SiH_2,PH,S) and Cyclic $C_nSi_{4-n}H_6$ (n=0-4) Compounds

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ABSTRACT

Ab initio molecular orbital theory is used to characterize the series of bicyclobutane-like compounds $C_nSi_{4-n}H_6$ (n=0-4), and the corresponding cyclobutenes. Structures and harmonic vibrational frequencies are predicted at the 3-21G(d) SCF level. "Bent" bond lengths are computed using the 6-31G(2d) basis set with the 3-21G(d) structures. Second order Møller-Plesset perturbation corrections are applied to the 6-31G(d) single point calculations in determining relative energies of isomers. Ring strain and heats of formation of these compounds are predicted via homodesmic reactions. A similar characterization of the series of three-membered rings X_2H_4Y (X=Si,C; Y=CH_2,NH,O,SiH_2,PH,S) is also presented. Here the molecular geometries and vibrational frequencies are determined at the 6-31G(d) level and again bent bond lengths are predicted using the 6-31G(2d) basis.

12D

Ab initio Study Including Electron Correlation of the Groundstate of SiS

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Silicon sulfide, SiS, is a molecule of much astrophysical interest. This molecule was the first celestial maser detected in the circumstellar envelope of a late-type carbon star. Although many experimental studies (optical spectral studies and microwave studies) of this molecule have been made, only a very few *ab initio* investigations have been performed. In this poster, we present results of a set of large-scale, multireference, configuration-interaction calculations on the groundstate potential energy curve of SiS. These calculations include over 1.2 million configurations. We also present calculated spectroscopic constants for this molecule and various one-electron properties.

12E

Correlated calculations of the spin density distribution in some silicon-containing radicals.

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Hyperfine coupling tensors for a number of radicals containing silicon, hydrogen and oxygen have been determined by means of *ab initio* molecular orbital theory. The differential effects of single and double excitations from a multiconfigurational, but spin-restricted, Hartree-Fock reference space have been investigated. An alternative approach including single and double replacements from an unrestricted Hartree-Fock determinant has also been tested. In each case the magnetic properties have been computed as simple expectation values of the appropriate operator over the correlated wavefunction. Some orbital relaxation effects are thus neglected.

Using extended basis sets, certain of the Frosch-Foley parameters for SiH are well reproduced. The calculated ^{29}Si isotropic and dipolar coupling constants in the silaformyl radical are in close accord with recent experimental data and the values for its more stable isomer, SiOH, substantiate the suggestion that this species has also been detected in matrix isolation by ESR techniques.

While the known isotropic splittings in the silyl radical, SiH_3, are reliably calculated when vibrational averaging is included, the present estimation of the anisotropic coupling at silicon is not in accord with the current experimental interpretation.

Some other SiH_n radicals and radical ions, such as SiH_4^+ and SiH_5, have also been investigated and magnetic hyperfine parameters reliably determined. The calculated coupling constants show only partial agreement with the limited experimental data available and indicate that some spectral assignments are questionable.

Similar calculations have also been performed to predict the magnetic properties of a number of unreported isoelectronic species and metastable complexes.

The research described herein has been supported by the Office of Basic Energy Sciences of the United States Department of Energy. This is Document No. NDRL-2972 from the Notre Dame Radiation Laboratory.

12F

Ab Initio Investigations of the Low-lying Excited States of Several Polyenes

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ABSTRACT

Results from Multi-Reference CI calculations will be presented for several low-lying states of a variety of polyenes, including butadiene, hexatriene, and octatetraene. Many of the interesting features encountered in studies of ethylene are also seen for the longer chain species, such as strong valence-Rydberg mixing and the possible involvement of non-vertical transitions. In addition, the question of whether the lowest singlet excited state is the allowed $\pi \rightarrow \pi^*$ transition (as expected on the basis of MO arguments) or is instead a nominally doubly excited state (as has been observed for longer polyenes) will be addressed. The qualitative natures of the various states will be discussed, and the trends observed in proceeding from ethylene to octatetraene along the series will be examined. Comparison will also be made with semi-empirical results for these systems, as well as with previous ab initio treatments.

12G

SPIN DENSITY CALCULATIONS ON FREE ATOMS

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Attempts to calculate accurate Fermi contact spin densities in free radicals by *ab initio* methods have often met with only modest success. It has generally not been clear to what extent the difficulties have been due to basis set inadequacies or to insufficient configuration lists. In an effort to quantify these effects, we have carried out benchmark numerical MCSCF calculations on all the first row atoms with open shell p-electrons. These are particularly demanding test cases due to large but nearly cancelling separate contributions from core and valence electrons, leaving relatively small net spin densities at the nuclei.

Radial functions were determined numerically to eliminate any questions about basis set inadequacies. Fitting to these results will then give a valuable guide in developing basis sets appropriate for spin density calculations in molecular systems. The importance of various configurations was evaluated by including them in MCSCF wave functions of different sizes and compositions. It was found that configurations representing spin polarization, orbital polarization, and electron correlation are all qualitatively necessary to correctly determine the spin density at the nucleus. The relative importance of each of these effects has been evaluated separately for core and valence electrons. The results provide insights into which configurations may be important in molecular calculations.

POSTER

CANCELLED

Systematic Studies of Molecular Vibrational Anharmonicity and Vibration-Rotation Interaction by Self-Consistent-Field Higher Derivative Methods. Applications to Asymmetric, Symmetric, and Spherical Top and Linear Polyatomic Molecules

D. Allen Clabo, Jr., Richard B. Remington, Wesley D. Allen,
Yukio Yamaguchi, and Henry F. Schaefer III

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Abstract

Recently developed analytic third derivative methods for self-consistent-field (SCF) wavefunctions have been employed for the calculation of cubic force constants analytically and quartic force constants by finite differences of third derivatives for a series of molecules which includes examples of asymmetric, symmetric, and spherical top and linear polyatomic rotational type. Harmonic vibrational frequencies, vibrational anharmonic constants, fundamental vibrational frequencies, quartic and sextic centrifugal distortion constants, vibration-rotation interaction constants, rotational constants with zero-point vibration and centrifugal distortion corrections, and vibrational and rotational ℓ-type doubling constants are reported, in excellent agreement with the available experimental spectroscopic data.

An efficient alternative to brute force CI: ArH^+ system.

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Short range part (1.5au<R<8au) of the potential energy curves of the 37 lowest excited states of ArH^{+*} have been calculated (ab-initio CI using the Polarised Atomic Orbitals (PAO's) technique (Ref 1)).

A simple analysis of the system shows that - apart from a few valence states (5 states) - most of the states can be described as consisting in a $(ArH)^{++}$ core plus a diffuse electron (32 states). The existence of two electronic states of the core ($^2\Sigma$, purely repulsive and $^2\Pi$ with a shoulder) gives rise to two families of $(ArH)^+$ states essentially parallel to the parent $(ArH)^{++}$ state.

This remark allows to drastically reduce the number of active orbitals of the CI (45 orbitals out of 70 CGTO's) as well as the size of the CI.

In addition, this remark leads to a direct interpretation of the existence of satellites in the blue wing of the Lyman-α line of H in an argon plasma.

Ref:
G.CHAMBAUD, M. GERARD-AIN, E. KASSAB, B. LEVY and P.PERNOT Chem. Phys. 90,271, (1984)

13B

THEORETICAL STUDY OF NITROUS ACID: EQUILIBRIUM GEOMETRIES, FORCE CONSTANTS, AND VIBRATIONAL SPECTROSCOPY

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An ab initio study of *cis* and *trans* nitrous acid was conducted at two different levels of theory (SCF and local MP4(SDQ)[1]) with a 6-311G** basis set. The equilibrium geometries were calculated at both levels of theory and compared with the experimental isotope substitution (r_s) values (Table 1). The MP4 values are in good agreement with experiment, although the N-O single bond stretch is underestimated by approximately 0.02 Å in each conformer. This fairly large error may be due to the neglect of the triple substitutions in these perturbation calculations.

The force constants were calculated at the MP4 reference geometries. After scaling the force constant matrix, the vibrational fundamentals were calculated and compared with the experimentally observed frequencies[2] (Table 2). These scaled frequencies are in very good agreement with the experimental frequencies. A fairly large scale factor (0.75) for the N-O bond values was needed to attain this level of accuracy in the calculated frequencies. The need for such a large scale factor is a consequence of the error in the N-O bond length.

TABLE 1. Geometry of HONO (bond lengths in Å, angles in degrees)

	cis HONO			*trans* HONO		
COORDINATE	SCF	MP4(SDQ)	EXP.[2]	SCF	MP4(SDQ)	EXP.[2]
1- NO STRETCH	1.309	1.3759	1.392	1.322	1.4052	1.432
2- OH STRETCH	0.951	0.9727	0.982	0.942	0.9632	0.958
3- N=O STRETCH	1.148	1.1859	1.185	1.141	1.1753	1.170
4- HON BEND	108.3	104.99	104.0	105.8	102.11	102.1
5- ONO BEND	114.1	113.11	113.6	111.9	110.63	110.7
6- TORSION	0.0	0.0	0.0	180.0	180.00	180.0

TABLE 2. Vibrational frequencies of *cis* and *trans* HONO (in cm^{-1})

	cis HONO		*trans* HONO	
FUNDAMENTAL NUMBER	SCALED FREQUENCY	EXPERIMENTAL FREQUENCY[3]	SCALED FREQUENCY	EXPERIMENTAL FREQUENCY[3]
ν_1	3465.94	3426.22	3602.19	3590.71
ν_2	1659.43	1640.52	1678.38	1699.80
ν_3	1294.91	NOT OBS.	1266.95	1263.18
ν_4	849.86	851.93	806.19	790.12
ν_5	615.63	NOT OBS.	598.92	595.62
ν_6	636.96	639.80	552.74	543.88

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3) C. M. Deeley and I. M. Mills, Mol. Phys., 45, 23 (1985).

13C

SHORT RANGE INTERACTIONS BETWEEN HYDROGEN MOLECULES

M D COOK and P J HASKINS

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The electronic structure of molecular hydrogen at high pressure has been the subject of a number of studies in recent years. High pressure hydrogen is of considerable interest in is own right, although to the theoretician it is of particular importance being the simplest neutral molecule and therefore an ideal test system.
Here we report a computational study of 3- and 4-body contributions to the intermolecular potential of H_2 at short separations. This has been carried out using SCF and Moller-Plesset many-body perturbation theory methods. Interactions between 2, 3 and 4 hydrogen molecules have been studied in a variety of geometries with intermolecular separations in the range 1.0 - 3.0 A° . Particular attention has been paid to linear chains, side-on orientations and the regular hexagon. The majority of the calculations have been carried out with the H_2 bond length fixed, although in a number of instances the bond length has been optimised at each separation. Preliminary SCF calculations (reference below) which predicted significant 3- and 4-body effects at close separations in the side-on orientation have been confirmed by extensive calculations at the fourth order Moller-Plesset level (single, double, triple, and quadruple excitations all included). The implications of these studies to calculations of the molecular to metallic phase transition pressure in solid hydrogen are discussed.

Reference: Haskins, P J and Cook, M D; in Shock Waves in Condensed Matter - 1985, edited by Y M Gupta (Plenum, New York, 1986), p 113.

/3D

IMPLEMENTATION OF ANALYTICAL ENERGY GRADIENTS AT THIRD AND FOURTH ORDER MØLLER-PLESSET (MP) PERTURBATION THEORY

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Fourth order Møller-Plesset perturbation theory is known to correct for a large part of electron correlation errors in a systematic manner. In order to calculate molecular properties at this level of theory in a routinely manner, the implementation of analytical gradients is desirable. We present the formulas for analytical MP3 and MP4 energy gradients and discuss their implementation. Calculated equlibrium deometries, dipole moments, harmonic vibrational frequencies, and infrared intensities are given at the MP3 and MP4 level of theory for a number of molecules. Formulas for analytical energy gradients of nth order Møller-Plesset perturbation theory are also presented.

13E

ANALYTICAL GRADIENTS TO FOURTH ORDER IN ENERGY FOR THE PCILO METHOD

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Although the semiempirical PCILO method is used extensively for determining molecular conformation, the geometry searches are still carried out without the use of analytical energy gradients. In this paper this deficiency is addressed. A complete diagrammatic formulation of the energy gradient to fourth order is presented for the PCILO method. Results as well as computational times for geometry optimizations on several comparatively large molecules are reported.

13F

NONADDITIVITY IN THE INTERACTIONS OF FE^{2+} AND FE^{3+} IONS WITH WATER

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Abstract for the
1987 American Conference on Theoretical Chemistry

July 1987

136

ABSTRACT

1987 American Conference on Theoretical Chemistry

THEORETICAL ANALYSIS OF ENZYME MECHANISMS IN CYSTEIN PROTEASES.

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Quantum mechanical calculations and macromolecular structural comparisons are used to study the enzymatic mechanisms of cysteine proteases. Although the enzymes papain and actinidin show a high degree of homology and extensive structural similarity, they have different specificities and may have different active site mechanisms. In particular, the role of an aspartic acid in the active site may be different, as suggested by experimental evidence which shows this residue to be important in papain but not in actinidin. Simulations of the proton transfer process between the Cys and His residues present in the active sites of both proteins are used to reveal the role of the protein environment in the determination of the mechanisms of these proteins. Results from ab-initio molecular orbital calculations including the evaluation of the effect of protein environment with the self consistent direct reaction field method are used to compare the mechanisms in the two proteins.

13H

FIELD-THEORETIC POTENTIAL-ENERGY CURVES FOR H_2 and F_2

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Energy corrections thru third order are reported for zeroth-order separated-pair wave functions. A BCS Ansatz is exploited to calculate the corrections with ordinary Feynman diagrams. The fractional occupancies appear as renormalized interactions and energy denominators. The MBPT calculation requires almost the same code as MBPT based on a determinantal Ansatz. However, the new MBPT may be applied even where ordinary particle-hole theory breaks down to every finite order. The results presented here illustrate this for the case of bond rupture.

Jahn-Teller Distortion in CH_4^+

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ABSTRACT

The Jahn-Teller effect in CH_4^+ has been studied extensively both experimentally and theoretically. The tetrahedral configuration of CH_4^+ has a triply-degenerate $^2T_2$ state which is subject to a Jahn-Teller distortion. In 1984, Knight et. al. provided direct experimental evidence for a C_{2V} ($^2B_1$) ground-state assignment for the cation using neon matrix ESR results.[1] This has led to a number of new theoretical studies.

The aim of the present study was to obtain a reasonably accurate representation of the three lowest states of CH_4^+, in the region surrounding the tetrahedral geometry and extending beyond the C_{2V} ground-state minimum of the ion. The potential energy surface is based on 6-31G** basis set results from MRSDCI calculations on the three lowest states over a wide range of geometries. Special care must be used in choosing an one-electron basis for the CI's, so as not to artificially bias the results toward one of the close-lying states. The method used to minimize this bias will be discussed.

To fit the potential energy data, a normal mode description was used to represent the distortions of the molecule and the three surfaces are fitted to a power-series expansion in the normal mode displacements from the tetrahedral configuration.

[1] L.B. Knight, Jr., J. Steadman, D. Feller, and E.R. Davidson, J. Am. Chem. Soc., 106, 3700 (1984).

14B

A New Algorithm for Solving Self-consistent Electronic Structure Equations

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ABSTRACT

A new algorithm for self-consistent electronic structure calculations has been developed. The algorithm is a synthesis of conventional electronic structure techniques with the pseudospectral method, a numerical approach used in hydrodynamic simulations of turbulence. The Hartree-Fock equations have been solved for the neo. atom[1], several diatomic molecules,[2] and the water molecule.[3] In all cases, quantitative agreement with conventional Roothaan calculations is obtained for various observable properties (force constants, equilibrium geometry, energy eigenvalues, dissociation energy). Timing results on a Cray X–MP indicate that rate enhancements of $O(10^3)$ can be expected for large basis sets. This is a consequence of the N^3 scaling of the algorithm with basis set size and of the elimination of two-electron integrals from the calculations.

[1] R. Friesner, Chem. Phys. Lett. **116**, 39 (1985).
[2] R. Friesner, J. Chem. Phys. **85**, 1462 (1986).
[3] R. Friesner, J. Chem. Phys., in press.

147

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14B

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[2] R. Friesner, J. Chem. Phys. **85**, 1462 (1986).
[3] R. Friesner, J. Chem. Phys., in press.

14C

Three Explorations of the Assumptions Behind and a Reappraisal of Semi-Empirical Molecular Orbital Methodology

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The needs for a new approach to semi-empirical molecular orbital methods are presented. Existing methods are evaluated in the context of evolving requirements and expectations. Three new approaches are examined: 1) a conventional ZDO method, modified to take advantage of recent advances in algorithms for ab initio calculations, 2) unparametrized neglect of integrals and 3) direct direct approximation of integrals. The results shed light on some of the fundamental assumptions and critical approximations behind current methods. The identification of specific types of integrals which are both critical for accuracy and computationally rate-limited suggests an approach to be taken for the future development of more flexable and more accurate approximate methods.

14D

CHARGE DENSITY TOPOLOGICAL EVIDENCE OF MOBIUS AROMATICITY IN HOMOTROPYLIUM CATION.

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The homotropylium cation **1**, one of the earliest claimed examples of an homoaromatic system,has always attracted a considerable amount of attention. There are only three reported structure determinations of potential homotropylium cations, i.e. the benzohomotropylium (**2**), the 1-ethoxyhomotropylium (**3**), and the 2-hydroxyhomotropylium (**4**) cations. The crystallographic data are consistent with an homoaromatic formulation of cation **4**, and indicate that any transannular bonding interaction between C_1 and C_7 in **2** and **3** must be very weak. While it is clear that the appropriate placement of electron donor substituents can invert the relative stabilities of the open (**1b**) and the closed (**1a**) forms of the cation, no definitive structural work has been reported for the parent unsubstituted cation **1**.

We report a reinvestigation of the parent cation and its 2,6-OH derivative **5** using *ab initio* molecular orbital theory. Full geometry optimizations within C_s symmetry constraints at both the RHF/3-21G and RHF/6-31G* levels definitely indicate the cyclooctatrienylium cation **1b** as the *global minimum* on the $C_8H_9^+$ potential energy surface, and that the homoaromatic structure **1a** is not even a stationary point. This has been confirmed by tracing the hypothetical reaction path for the conversion of **1a** into **1b**. The energy values obtained by relaxing all the geometrical variables at fixed values of the C_1-C_7 distance decrease monotonically in the range from 1.500 Å to the equilibrium value, 2.284 Å (6-31G*). The effects of electron correlation on the potential shape have been estimated by single point MP2/6-31G//RHF/6-31G* calculations and have been extrapolated to MP2/6-31G*//RHF/6-31G* level by means of additivity criteria of basis set and electron correlation effects. The latter technique has proved to be successful for related systems, e.g. the homocyclopropenylium cation whose puckered form is predicted to be more stable than the planar one by 11.1 kcal/mol, to be compared with the exact MP2/6-31G* value of 11.8 kcal/mol.

The minimum energy geometry of **5** is consistent with an homoaromatic formulation of the substituted cation as, at variance with **1b**, a bond path links the two bridgehead carbons, whose distance amounts to 1.544 Å. The charge density at the bond critical point (bcp) is .202 e/au^3 in **5** and is lowered to .082 at the C_1-C_7 midpoint in **1b**. The bridge bonds in **1b** present both an high bond order (1.03)[1] and an high overlap (.990) with the vicinal CC bonds despite the unfavourable value of the geometrical puckering angle (116.1°). All these facts point out the involvment of the methylene group in π conjugation. The carbon atom energies (obtained by integrating the kinetic energy density in the atomic basin enclosed by zero flux surfaces in $\nabla\rho$), the charge density values at carbon nuclei, and the position of the C-H bcp point out quantitatively that the positive charge is maximally concentrated at C_1,C_3 carbons in **1b** and at C_2,C_4 carbons in **5**. Besides these carbons present, in their valence shell charge concentration, the characteristics holes which denote the preferred position of attack for incoming nucleophiles, as do carbons formally bearing the positive charge in conventional carbocations. The reported data nicely agree with the lack of an homoaromatic bond in the cation **1**, thereby strengthening the correspondence between bond paths and usual chemical bond concepts.

It can be concluded that the homotropylium cation **1**, which has 69% of the aromatic character of the corresponding tropylium cation (based on their 3-21G isodesmic bond separation reactions), can be best regarded as a *Möbius aromatic*, instead of a conventional Winstein homoaromatic cation.

14E

COMPUTATIONAL STUDIES OF DITHIATRIAZENES

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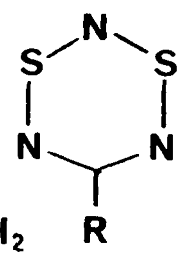
A more detailed understanding of the relationship between molecular and electronic structure is crucial to the continuing development of main group inorganic chemistry and in particular, sulphur-nitrogen cycles. This poster presents the results of *ab initio* molecular orbital and electron correlation computations on model dithiatriazenes (RCN_3S_2):

S_0 or T_1

C_{2v} or C_s



R = H, NH_2
F, BH_2

The discussion will focus on the change in the singlet-triplet energy gap with different R (R = H, NH_2, F, BH_2) and on the rationalization of this electronic effect in frontier orbital terms. The susceptibility of singlet RCN_3S_2 rings to electronic and nuclear distortions driving a lowering of the framework symmetry from C_{2v} to C_s will be considered. The roles of π and σ orbital interactions in such distortions will be examined.

Financial support of this research through grants from the Natural Sciences and Engineering Research Council of Canada (NSERC) is acknowledged.

14F

DIMENSIONAL PERTURBATION THEORY:

A NEW APPROACH TO CALCULATING ELECTRONIC STRUCTURE

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and

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Abstract:

We show that perturbation expansions in 1/D, the reciprocal of the Cartesian dimensionality of space, can yield extremely accurate values for energy levels and important qualitative information about electron correlation. Results are presented for the two-electron atom.

146

CORRELATION SCALING AND BALANCED BASIS SETS FOR POTENTIAL ENERGY SURFACE CALCULATIONS

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Basis sets ranging from minimal to triple zeta with multiple polarization sets and diffuse functions are tested for their ability to consistently reproduce bond energies, heats of formation, reaction energy differences, and barrier heights for small molecules (no more than two heavy atoms) in the first four rows of the periodic table. The reactions studied are primarily hydrogen transfer reactions, and comparisons of the energy differences and barrier heights are also made with several semi-empirical methods and with experiment where possible.

14H

THEORETICAL ORGANOMETALLIC CHEMISTRY

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An accurate, compact basis set for the total geometry optimization of transition metal organometallics will be reported and the results for $Cr(CO)_6$, $Fe(CO)_5$, $Ni(CO)_4$, $Cr(C_6H_6)_2$, $Fe(C_5H_5)_2$, $Ni(C_4H_4)_2$, $Cr(NO)_4$, $C_5H_5Mn(CO)_3$, and $C_6H_6Cr(CO)_3$ will be described. Both basis set and electron correlation problems will be discussed. A calculation of the reaction path for the oxidative addition of H_2 to square planar cis-$RhCl(CO)(PH_3)_2$ will be described. This theoretical calculation mimics an experimental reaction in which the kinetic product is the isomer with H trans to CO while the thermodynamic products is the isomer with the H trans to Cl.

15H

AB INITIO CALCULATION OF RESONANCE RAMAN INTENSITIES

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Resonance Raman spectroscopy has become a popular tool for the study of biomolecules, and for probing conjugated macromolecules, some of which can become conducting polymers if doped properly. The experimental and theoretical study of short polyenes as model compounds is of great interest since more detailed information can be obtained from smaller systems.

The resonant Raman spectral intensities are largely determined by an excited state surface that has a large moment for transition from the ground state, provided that the incident photon frequency is near the frequency of the transition. The intensity into normal mode i depends on the gradient of the excited state potential energy surface with respect to mode i mode, and the frequency of mode i. This result, given by Heller [1], can also be derived compactly from perturbation theory by using a form similar to that used in the Hylleraas variation-perturbation method [2]. In the ab initio calculations, the gradient differences are used since the SCF forces of the ground state are nonzero at the reference geometry. The reference geometries were chosen such that they are close to the true equilibrium geometry, using SCF geometries that are corrected by the method of Pulay et al. [3] to account for systematic errors .

Relative resonance Raman intensities wil be presented for butadiene, *cis* and *trans*-hexatriene, and for the all *cis* and all *trans*-octatetraene. Comparisons will be made with the resonance Raman spectra of these compounds and *cis* and *trans*-polyacetylene. The scaled quantum mechanical force fields [4] and normal modes for these short polyenes will be compared to those proposed for the polyacetylenes.

1. E. J. Heller, in Potential Energy Surfaces and Dynamics Calculations, edited by D. G. Truhlar (Plenum, New York, 1981) p. 103.
2. E. A. Hylleraas, Z. Phys. **65**, 209 (1930).
3. P. Pulay, G. Fogarasi, F. Pang and J. E. Boggs, J. Am. Chem. Soc. **101**, 2550 (1979).
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/5B

VALENCE QUANTUM MONTE CARLO WITH AB INITIO EFFECTIVE CORE POTENTIALS*

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In quantum Monte Carlo (QMC) the need for a valence-only or effective core potentials (ECP) approach is perhaps even greater than in conventional ab initio methods, because the innermost electrons are responsible for a sharp increase in the computational time required for heavy-atom systems. We have analyzed the Z dependence of CPU time for the QMC technique and arrived at $Z^{6.5}$. A very different picture emerges when treating only the valence electrons. We have determined the CPU dependence to be $(Z^{eff})^{3.4}$. This is a significantly lower power than $Z^{6.5}$. More importantly, however, unlike Z, Z^{eff} remains a small number for all atoms. Another difficulty at large Z in all-electron calculations stems from the fixed-node approximation. Although the fixed-node error is typically a very small percentage of the total energy, when the total energy is large the fixed-node error can be a significant fraction of the dissociation energy. Treating only the valence electrons leads to a smaller calculated energy and eliminates the core nodes. This has the effect of reducing the fixed-node error to well below the dissociation energy.

We have developed a theory of effective core potentials within the QMC method and applied it to the determination of electron affinities(EA), ionization potentials(IP) and dissociation energies(D_e) for the one- and two-effective-electron systems Li, Na, Mg, NaH and Na_2. In all cases ECP-QMC results are found to be as accurate as previous all-electron results. In particular, the calculated quantities in eV (versus experimental values) are: EA(Li) = 0.611±0.020(0.620), EA(Na) = 0.555±0.021(0.546), IP(Mg) = 7.637±0.026(7.646), D_e(NaH) = 1.954±0.073(1.971), and $D_e(Na_2)$ = 0.746±0.020(0.747). In addition, the statistical precision obtained surpasses that which can be readily achieved in all-electron QMC calculations on these systems.

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†Also, Department of Chemistry, University of California, Berkeley.

/5C

THE CONVERGENCE OF PROJECTED UNRESTRICTED HARTREE-FOCK MØLLER-PLESSET SERIES

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Abstract

The problem of spin contamination in the Unrestricted Hartree-Fock Møller-Plesset (UMP) series is examined, using our full CI programs to generate the series to high order. A scheme involving spin projection of the MP series wavefunctions has been devised, which shows a substantial improvement over the regular UMP series. Practical schemes for implementing reasonable approximations to the scheme are discussed. It is shown that it is possible to perform a projected second order calculation at the same cost as regular fourth order Møller-Plesset theory, but with substantially better results in cases where spin contamination is severe.

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15D

AB INITIO STUDY ON STRUCTURES AND REACTIVITY OF BERYLLIUM COMPOUNDS

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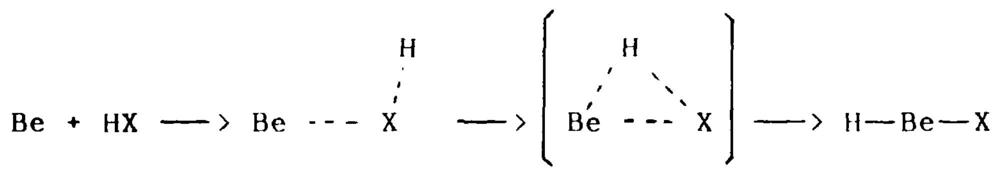
The chemical reactivity for the systems containing Be atom is investigated by using the *ab initio* molecular orbital method. The molecular structures and potential energy surfaces are calculated by the analytical gradient method for the closed-shell SCF wavefunctions and the reaction energies are estimated including electron correlation (SDCI and MP3).

The Be containing bonds have relatively strong covalency as well as the ionic nature, although the other alkali-earth elements behave as divalent cation in most of chemical systems. It is interesting to explore the nature of forming bond with Be atom in the light of the amphoteric character of Be atom. Since the bond formation by the insertion reaction such as

$$Be + H_2 \longrightarrow BeH_2 \qquad (1)$$

is symmetry forbidden and hence has large energy barrier, the promotion of the electrons from 2s orbital to 2p orbital is essential to form Be-H bonds. By replacing one hydrogen to another atom or radical X (X = NH_2, OH, F and Cl), the mechanism of the insertion reaction becomes the two-step reaction. The charge transfer complex is first formed, and the hydrogen migration leads to form the divalent Be compound ;



(2)

The stability of CT complex and the barrier height of the second step vary strongly depending on the reactant group X. The strength of Be - X bond can be discussed with the heat of formation, the stretching frequency, and the electronegativity of X.

The interaction between Be and O atoms is found to be rather strong among the systems which we have studied in reaction (2). As the first stage to explore the behavior of alkali-earth elements in the aqueous solution, the interaction of Be and H_2O is studied for $Be(H_2O)_m$ and $[Be(H_2O_n]^{2+}$. Furthermore, the detailed mechanism of the solvolysis of neutral Be in acidic condition is also studied theoretically in molecular level. The result shows that the difference of the stabilization energies for saturated hydration between neutral Be (m = 3) and Be^{2+} ion (n = 4) plays an important role on the hydrolysis of Be atom.

15E

SHORT RANGE INTERACTIONS BETWEEN NITROGEN MOLECULES

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SCF and Moller-Plesset many-body perturbation theory calculations are reported for a variety of geometrical arrangements of up to 4 nitrogen molecules. These studies are concerned only with the close-in repulsive region and concentrate on intermolecular separations in the range 1.8 - 3.0 A°.

Particular geometries studied include three molecules in a side-on equilateral triangle arrangement and a regular N_6 hexagon. It is shown that in the side-on orientation 3-body contributions to the interaction potential become significant at separations below 2.8 A° . In the equilateral triangle geometry the 3-body energy results in a softening of the total pair interaction which increases in magnitude with decreasing separation. The regular hexagon structure is shown to be the lowest energy configuration for 3 X N_2 at bond centre separations of ≈2A°. Possible structures for solid nitrogen at high pressure are discussed in the light of these results. Bond length variations in nitrogen are also reported as a function of intermolecular separation and orientation.

15F

Simultaneous Optimization of Molecular Geometry and Wavefunction in the Finite Basis Hartree-Fock Method

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In MO calculations, a theoretical equilibrium geometry is usually obtained by guessing an initial geometry and then-

(1) Minimizing the energy at the current geometry by varying the MO coefficients.

(2) Calculating the gradient of the energy with respect to the internal coordinates, and using it to alter the geometry. If the gradient is sufficiently non-zero, go back to (1).

The feature of *separately* varying the wavefunction and geometric parameters is somewhat artificial, as they are both simply variables upon which the energy depends. We have therefore derived equations appropriate for the *simultaneous* optimization of both sets of parameters in the finite basis Hartree-Fock method. Results from the computer implementation of this new procedure will be discussed.

15G

ANALYTICAL CALCULATION OF MOLECULAR PROPERTIES USING FLOATING GAUSSIAN ORBITALS

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Jan Almloef, Department of Chemistry, University of Minnesota, Minneapolis, Minnesota

The calculation of molecular wave functions and properties using floating Gaussian orbitals is discussed. In particular the analytical determination of first- and second-order properties is described. Hartree-Fock calculations at the double-zeta (DZ) and double-zeta plus polarization (DZP) levels are presented for a series of molecules. These calculations show that by floating the basis functions one obtains a significant improvement in the calculated properties.

Calculations using floating DZ basis sets give geometries and force constants comparable to those obtained at the fixed DZP level, while the calculated dipole moments and polarizabilities are superior to those obtained using fixed DZ or DZP basis sets. The dipole moments are in excellent agreement with experiment while the polarizabilities are 10 - 20 % below the Hartree-Fock limit.

Adding one set of polarization functions to floating DZ basis sets has no effect on the calculated dipole moments and polarizabilities, but results in geometries and force constants closer to the Hartree-Fock limit.

15H

Are Bicyclo[1.0.0]butenes Isolable?

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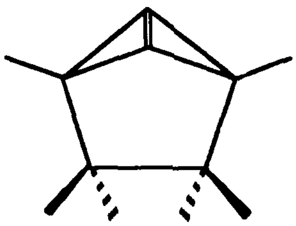
Bicyclo[1.1.0]but-1(3)-ene (**1**) was found to be a minimum on the C_4H_4 potential surface only when d-orbitals were included in the basis set. Earlier structures found by

1

Pople and Schleyer (STO-3G) and Wiberg (4-31G) were shown to have one imaginary frequency. However, the 6-31G* and MP2/6-31G* structures both gave all real frequencies.

The structure of tricyclo[2.1.1.0^{5,6}]hex-5(6)-ene (**2**), a derivative of bicyclobutene



2

reported to have been trapped by Szeimies (Munich), was optimized with the 3-21G, 6-31G* and MP2/6-31G* basis sets. Both the 3-21G and 6-31G* structures yield an imaginary frequency. However, in an MP2/6-31G* vibrational analysis the imaginary frequency of the smaller basis sets became real. Thus the tricyclic structure is predicted to be stable in agreement with experiment. Hence bicyclobutene itself, which should be less strained than the tricyclic derivative, is expected to be observable.

16A

A Unitary Coupled Cluster Method

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The linear realization of a unitary coupled cluster method has been derived and implemented for small molecules. The equations are formulated entirely within a Lie algebra, and so size-inconsistent terms are not introduced at the correlating level.[1] Mapping from the uncorrelated model space to the correlated model space is effected by a single wave operator. The theory supports a multiconfigurational reference function, and allows both for relaxation and correlation effects (e.g., internal, semi-internal, and external excitations). The pilot program uses unitary group operators,[2] and is fully tied to the system of electronic structure programs available in this laboratory. An illustrative calculation on the well-studied Be insertion into H_2 gives agreement with the full CI result for the vertical excitation energy of the two lowest $^1A_1$ states within 0.4 kcal/mol across the transition region.

1 H. Primas, Rev. Med. Phys. 35, 710 (1963); Helv. Phys. Acta 34, 331 (1961).

2 A. Banerjee and J. Simons, Int. J. Quant. Chem. 19, 207 (1981); J. Chem. Phys. 76, 4548 (1982).

16B

OPTIMIZED TRIAL FUNCTIONS FOR QUANTUM MONTE CARLO STUDY OF H_4*

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In recent years the fixed-node quantum Monte Carlo method (FNQMC) has been successfully applied to the calculation of electronic energies of small molecules. The attractive feature of this method is that with a modest basis set and often a single-Slater determinant one typically recovers over 90% of the correlation energy.

Because the simulation is dominated by a trial function that fixes the nodal positions, a good trial function is essential in order to obtain an accurate result. It is often chosen to be an *ab initio* approximate Hartree-Fock wavefunction in which case the many-electron nodes are established without consideration of electron correlation. By incorporating a Jastrow factor the variational energy is improved, but this nodeless function does not improve the nodes of the system. Ideally, the Slater determinant needs be re-optimized in the presence of the correlation factor.

We have developed an algorithm to optimize trial function parameters (linear coefficients, non-linear exponential factors, and parameters of the correlation function) based on a random walk procedure. In order to obtain accurate energies for excited states, we introduce a projection operator method based on group theory to constrain the optimization process. It effectively distinguishes all the states of a given symmetry. We also apply the Young tableaux of permutation group theory to facilitate the treatment of fermion properties and multiplets.

Using an optimized trial function, we are studying pyramidal H_4 at the maximum ionicity excited state[1] (MIES) and other geometries relevant to understanding decomposition pathways in this system. The calculated potential energies show 0.6-0.8 ev lowering compared to a previous study[1]. In a separate multi-configuration *ab initio* study we have determined that there is a pathway without a barrier for $H_2(B)$ approach to ground state $H_2(X)$. Work is in progress to fully characterize the first-excited state of the H_4 system and its coupling to the ground state.

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1 C. A. Nicolaides, G. Theodorakopoulos, and I. D. Petsalakis, J. Chem. Phys. **80** (4), 1705 (1984).

16C

ENERGIES AND WIDTHS OF THE LOWEST $^1\Sigma_g^+$ STATES OF H_2

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Positions and widths for the lowest $^1\Sigma_g^+$ doubly excited autoionizing states of H_2 at several internuclear separations have been obtained by the calculation of Siegert eigenvalues. This approach involves the direct computation of the complex resonance energy in a basis set of both real and complex Slater orbitals. When the complex orbitals are centered between the two atoms, the numerical results are in fair agreement with previous theoretical treatments, although the present width does not rise quite as much for larger internuclear separations. In addition, the present results are somewhat sensitive to the basis set parameters; the details will be discussed.

16D

The Performance of an Advanced Vectorizing Preprocessor on Some Typical Quantum Chemistry Codes.

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The advent of computer architectures based on vector pipelines and parallel CPU's has led to a very strong dependence of computational performance on the detailed structure of Fortran codes. At the same time the opportunity to carry out computations on a variety of remote supercomputers has forced researchers to remove computer specificity from their Fortran codes. This portability versus performance dilemma is important to the computational chemistry community, as the effort required to redesign codes in order to achieve efficiency on a particular architecture often detracts from our ability to generate new, more powerful codes.

One hope for resolving this dilemma resides in the development of software which can restructure portable Fortran codes for efficient execution on a particular target architecture. The KAP205 utility from Kuck & Associates, Inc., which is a product designed to restructure Fortran codes for the CDC Cyber 205 computer, has been under BETA site testing at Langley. It is expected that a modification of this utility will be made available as a standard part of the ETA supercomputer software.

KAP205 utilizes data dependence graphing to enable "intelligent" decisions on vectorization. It inverts nested DO loops in order to achieve long vector lengths, "strip mines" vector operations when vector lengths exceed the architecture limit of 65,536, and inserts explicit vector extensions of Fortran to take advantage of the Cyber 205 instruction set. The output of the utility is an annotated program listing and a modified copy of the Fortran source code. The annotated listing contains questions about the code which, if answered, could result in more efficient vectorization during a subsequent iteration of the utility.

During the period leading up to the 1987 American Conference on Theoretical Chemistry the authors will be carrying out an analysis of the performance of the KAP205 on portions of two sets of quantum chemistry codes. The MELD package, from E. R. Davidson and collaborators, is a modern set of conventional quantum chemistry codes which has been designed to be very portable and has been exercised on a variety of computers. The other package, HYDRA, from Paul Saxe and Byron Lengsfield includes MCSCF, GUGA CI, and energy derivatives capabilities. HYDRA was originally implemented for the CRAY X-MP. Results of using the KAP205 utility on both the MELD and HYDRA packages will be presented at the conference.

16E

A Comparative Evaluation of Some Ortho Directing Groups for Cubane

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ABSTRACT

We have investigated the basis for the activating and directing effects of an initial amide substituent in the subsequent functionalization of cubane via a lithiated intermediate (the "ortho lithiation procedure"). An ab initio self-consistent field computational approach was used. We find at least three mechanisms to be involved:

(1) Enhanced acidity of a hydrogen on an adjacent carbon;

(2) Stabilization of the subsequent 2-lithio derivative through an interaction between the lithium and the amide group; and

(3) Creation of a channel of strongly-negative electrostatic potential leading to the liated carbon, rendering it susceptible to electrophilic attack.

We have used the above described method to analyse the effectiveness of four different functional groups in their ability to activate "ortho lithiation" on strain cubane systems; They are, (1) oxazoline group (2) trifluromethyl group (3) methyl group and (4) nitro group. Molecular electrostatic potential results indicate a build up of a strong negative electrostatic potential leading to the lithiated carbon, which is susceptible to electrophilic attack, and the magnitude of this minima closely related to the effectiveness of the ortho directing group.

/: F

Evaluation of Line Strengths for Spin-forbidden Transitions: Application to CH^-

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When the spin-orbit part of the microscopic Breit-Pauli interaction (H^{so})

$$H^{so} = (-e^2/2mc^2)\left(\sum_{i,K} (Z/r_{Ki}^3)\ \mathbf{l}_i(K)\cdot\mathbf{s}_i + \sum_{i\neq j} (1/r_{ij}^3)(\mathbf{r}_{ij}\times\mathbf{P}_i)\cdot(\mathbf{s}_i+2\mathbf{s}_j)\right)$$

is included in the molecular Hamiltonian, the eigenstates of the Hamiltonian cease to be pure spin states. The mixing of states is calculated using first order perturbation theory. The first order wave function Ψ_I^1 is obtained directly from the set of simultaneous linear equations [1]

$$(H^0 - E_I^0)\Psi_I^1 = H^{so}\Psi_I^0$$

where Ψ_I^0 and Ψ_I^1 are expanded in a configuration state function (CSF) basis. This approach avoids the costly determination of the zeroth order eigenfunctions for the virtual states. The zeroth order wave function for the states of interest (bound states) are calculated using a large scale *ab initio* state averaged MCSCF/CI approach.

CH^- has two bound states, the $X^3\Sigma^-$ ground and the $a^1\Delta$ excited states. The $a^1\Delta$ state couples to $^3\Pi$ states in the continuum through the Breit-Pauli interaction. Also, the $X^3\Sigma^-$ couples to $^1\Pi$ states in the continuum. The radiative lifetime of the spin forbidden $a^1\Delta$ to $X^3\Sigma$ transition is calculated and compared with experimental results[2]. The extremely difficult job of calculating the zeroth order eigenfunctions for the continuum Π states is avoided.

[1] S.J.Havriliak and D.R.Yarkony, J. Chem. Phys. **83**, 1168 (1985)

[2] M.Okumura, L.I.Yeh, D.Normand, and Y.T.Lee, J. Chem. Phys. **85**, 1971 (1986)

166

A Self Consistent Field Study of the Watson-Crick and Non-Watson-Crick Base Pairs

By

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ABSTRACT

In normal Watson-Crick base pairing scheme, adenine-thymine and guanine-cytosine (A-T and G-C) base pairs are formed, but under certain conditions, the enol tautomer of guanine can pair with uracil (U) and the imido tautomer of adenine can pair with cytosine. Base analogs can also substitute for naturally occurring bases in DNA resulting in mutations. The imino tautomer of N^4-aminocytidine (C^{AM}) has been shown to cause A-T to G-C transitions. To account for this transition two different pathways are proposed. The degree of mutagenicity of N^4-aminocytidine has been shown to be equal to the ratio of the rare imino tautomer in solution, but the imino tautomer of N^4-hydroxcytidine (C^{OH}) has been shown to exist in a 10/1 imine/amine ratio in solution and does not induce A-T to G-C transitions. Ab initio SCF calculations were performed on substituted and unsubstituted nucleic acid bases and their hydrogen bonded base pairing schemes using STO-3G and 3-21G basis sets. Localized Molecular Orbitals (LMO's) obtained from the Partial Retention of Diatomic Differential Overlap (PRDDO) method are employed to examine the changes occuring between the bonding patterns for the individual bases and the hydrogen bonded base pairs. The relative stabilities and LMO's for the Watson-Crick and Non-Watson-Crick base pairing schemes for the substituted and unsubstituted nucleic acid bases are G-C^{AM} > A-C^{OH} G-C > G-C^{OH} > A-C > A-T > A-U >> A-C^{AM} and their biochemical implications will be reported.

.16H

Ab initio Studies of the Structure and Energy of the $(H_2)H^-$ Complex

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The $H_2(H^-)$ complex was examined using various levels of Møller-Plesset Perturbation Theory (MPPT). *Ab initio* interaction energies were calculated through the fourth-order MPPT (MP4) level of theory. The best basis set yields an interaction energy, relative to H_2 and H^-, of ~ 1.2 Kcal/mol, at the MP4 level. Analytically optimized geometries at the SCF and MP2 levels are reported. The weak vibrational stretching mode of the H^- in the complex was investigated. The potential energy surface in this mode supports two vibrational levels. The weak stretching modes of the isotopically substituted complexes, $HD(H^-)$ and $H_2(O^-)$ were also analyzed. The surface crossings of $H_2(H^-)$ and H_3 at pertinent geometries were found, and their relevance to electron detachment in $H_2 + H^-$ collisions will be discussed.

17A

Selected Properties of Be_x ($x \leq 75$) in Ab Initio Model Approximations

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Abstract

Ab initio self-consistent field calculations are reported for several electronic states of beryllium clusters comprised of 13, 19, 21, 33, 39, 51, 57, 63, and 75 atoms. The clusters correspond to the second through tenth coordination spheres of a central Be atom with internuclear separations taken from the lattice constants of the bulk metal. Effective core potentials have been employed to replace the 1s core electrons, thereby reducing the complexity of the calculation. In addition, the use of the full point group symmetry of each cluster results in substantial reductions of the numbers of two-electron integrals that must be computed and processed. Properties calculated for each electronic state include binding energy, orbital energies, electric field gradient, nuclear-electron potential, diamagnetic shielding constant, second moments, and Mulliken populations. Overall net charges, second moments, and nuclear potentials are found to be unchanged in the larger clusters, indicating bulk behavior. Calculated ionization potentials increase with cluster size and approach the work function of Be metal.

17B

THEORETICAL INVESTIGATIONS OF DIATOMIC DICATIONS: THE NeN^{2+} DICATION

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Doubly and even higher charged diatomic ions have recently been found experimentally as metastable species having lifetimes of several μ-seconds in spite of their enormous inherent Coulomb repulsion. Quantum chemical calculations show that the potential curves of these ions are characterized by substantial barriers which prevent the thermochemically favored charge separation reaction. Among the interesting aspects of multiply charged cations is that the removal of two electrons does not necessarily mean weaker bonding. On the contrary, dicationic bonds may even be stronger compared to their neutral counterparts. In the extreme case, this leads to bound dicationic species while the corresponding neutral molecules do not exist. The most exciting examples of this effect are bound diatomics containing light noble gas atoms, like He or Ne. Using NeN^{2+} as a prototype the properties of such ions will be discussed.

178*

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HELIUM CHEMISTRY - STRUCTURES AND STABILITIES OF THEORETICALLY PREDICTED STABLE AND METASTABLE HELIUM COMPOUNDS

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Abstract:
Quantum mechanical investigations with inclusion of correlation energy show that He may form very strong bonds with carbon in doubly charged dications such as $HeCCHe^{2+}$. The investigation of small dications in different electronic states shows that the main driving force for a strong helium bond is not the positive charge, but rather the low-lying empty orbitals of the binding fragment. Thus, the theoretically predicted helium bond lengths in $HeCCHe^{2+}$, $HeNNHe^{2+}$, $HeOOHe^{2+}$ increase drastically in the order 1.085 Å, 1.359 Å, 2.231 Å, since the number of occupied orbitals is increasing. This trend is opposite to what is found for the isoelectronic neutral hydrogen compounds HCCH, HNNH, HOOH. Recognizing the decisive influence of the electronic structure on He bond formation it was possible to calculate and predict a stable, neutral He compound, i.e. HeBeO. Also NeNeO and ArBeO are predicted to be stable, observable molecules. The stability towards dissociation in HeBeO, NeBeO, and ArBeO is theoretically found as 3.0 kcal/mol, 2.5 kcal/mol, and 7.3 kcal/mol, respectively.

Bonding in these compounds is investigated by anlysis of the electron density distribution $\rho(\underset{\sim}{r})$ and its associated Laplace field, the Laplace concentration $\nabla^2\rho(\underset{\sim}{r})$. Covalent He bonds are found in some strongly bound cations, whereas closed-shell interaction dominates in HeBeO and in the weakly bound cations.

17C

The Electronic and Vibrational Energies of Two Double-Minima $^3\Sigma_u^+$ States of He_2

by

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ABSTRACT

The potential energy curves for the $^3\Sigma_u^+$ states of He_2 which correspond to the interactions of He $1s^2$ ^1S with He 1s2s ^3S and He1s2s ^3S with He 1s2s ^3S are obtained from second order configuration interaction calculations which themselves are based on a multiconfiguration self consistent field calculation. The basis set includes functions obtained by optimizing the dipole-, quadrupole- and octapole-polarizability of the ^3S atom and the dipole and quadrupole polarizabilities of the ground ^1S atom. For the lowest $^3\Sigma_u^+$ state we agree to within about 4 cm^{-1} with the observed vibrational energy level spacings, and agree nicely with the position and depth of the short range minimum deduced from spectra. We also obtain a potential hump at intermediate separations whose main features agree very well with those obtained from scattering experiments. The potential curve exhibits a van der Waals minimum about 3.82 cm^{-1} deep at about 11.6 a_o. The excited $^3\Sigma_u^+$ state has a deep metastable well at small internuclear separations as well as a well in the intermediate region which is about 3430 cm^{-1} deep.

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170

Triplet Potential Energy Surface of Si_2H_2

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Binkley and Luke et al. reported that the global minimum on the triplet potential energy surface of Si_2H_2 is not planar silasilene (C_{2v}: $^3A_2$) but bent silasilene (C_s: $^3A''$). However, the inclusion of zero-point vibrational energies reverses the relative energetic order between the bent and planar structures within the Hartree-Fock (HF) approximation, because the energy difference between these two structures is less than 0.2 kcal/mol at the HF level. This result is consistent with those obtained by Lischka and Koehler, and Kalcher et al. The effect of electron correlation at the planar structure is also larger than that at the bent one. Therefore, planar silasilene should be the global minimum on the triplet energy surface, though the planar structure is only 2 kcal/mol lower than the bent one at the highest computational level (MP4(SDTQ)/6-31++G(d,p)//HF/6-31G(d,p)).

Binkley also obtained twisted disilyne as a triplet minimum. However, it is unstable to HF internal perturbation. On the other hand, trans-bent disilyne is found to be apparently more stable than twisted disilyne by about 10 kcal/mol (HF) or 6.2 kcal/mol (fourth-order Moller-Plesset perturbation theory), but it is also unstable to HF internal perturbation. The ground states of these two structures have to be described mainly by two electronic configurations. Surprisingly, the energy difference (6.6 kcal/mol) between these two structures at the Full Optimized Reaction Space (FORS) MCSCF level, whose active space includes all valence orbitals, is similar to those obtained by the single configuration-based perturbation methods.

17E

Ab Initio and Semi-Empirical Molecular Orbital Calculations on Models for the Active Sites of Blue Copper Proteins

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We have carried out series of molecular orbital calculations on models for the active sites of the blue copper proteins stellacyanin and azurin. The largest models feature Cu(II) ligated by two imidazoles (histidine), dimethyl-thioether (methionine), methyl-thiolate (cysteine) and, in the case of azurin, formaldehyde (glycine); smaller models used ammonia in place of the imidazoles and had the methyl groups replaced by hydrogen atoms. Ab initio calculations (UHF, ROHF) employed effective core potentials on Cu, S, O, N, and C and basis sets of double-zeta plus polarization quality. Calculations on the electronically excited states (ROHF-CI) were carried out with a semiempirical INDO/S method parametrized to include transition metal atoms.

Presentation of the results will focus on the calculated spin distributions for the different model sites; the effects of geometrical distortions in the coordination sphere; the roles of the weakly ligated methionine and glycine residues ; and an attempt at detailed assignments of the optical spectra.

17F

Theoretical UV and MCD Spectral Data

For The Hydrolysis of Cis-Platin and Acetamide

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Abstract: Species resulting from the hydrolysis of cis-$Pt(NH_3)_2Cl_2$ with acetamide and its iminol tautomer have been investigated theoretically using the relativistic and non-relativistic charge-iterated extended Huckel molecular orbital methods. Transition energies, molar absorption coefficients, and MCD B terms derived from theory are presented using UV and MCD spectra plotting software program designed by the author. Relationships to base pairing and binding interactions are made with adenine. The electronic absorption and MCD spectra of all complexes are predicted to exhibit ligand field and charge transfer transitions arising from excitations out of the occupied Pt 5d orbitals and ligand orbitals of n and π type into the unoccupied Pt 5d and ligand π^* type orbitals. These transitions are expected to yield intense d->π^* and π->π^* absorptions in the UV spectral region. Optimized geometries and transition state have been located for acetamide and its iminol tautomer using the GAUSSIAN 82 program. (This research is supported by the ACS-PRF.)

176

Quest for Neutral Homoaromaticity: An MNDO Study on Annellated Semibulvalenes

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A neutral system which was considered to have the potential to exhibit homoaromaticity is the symmetric transition structure in the Cope rearragnement of semibulvalene. However, this strucutre has been shown to be about 5 kcal/mole above the stable localized structures. We have performed calculations on a bis-annellated semibulvalene which indicates that the symmetric form is now the stable, low-energy strucutre. We proposed this molecule as a new potential neutral homoaromatic system. Possible explainations of the stablization of this system will be discussed.

We have also examined the effects of singly annellating the semibulvalene, where the two localized structures are no longer equivalent. The energies of these structures provides a method for studying the competition between ring strain and the formation of double bonds at bridgeheads in small rings (anti-Bredt).

17H

A PES FOR THE Li + HCl REACTION

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The potential energy surface for the Li + HCl reaction has been calculated by performing UHF/CI ab initio computations for a large number of molecular geometries. Accuracy of calculated values has been checked by comparing their stationary point values with those computed when extending the basis set and including all CI corrections up to the fourth order. Despite the increased dimension of orbital and CI spaces, computed and experimental bond energies still differ of about 10%.

To make calculated values suitable for dynamical studies, constraints on diatomic asymptotes and transition state energies have been introduced. All ab initio values have been lowered to reproduce the dissociation energy of the HCl diatom and the profile of the exit channel has been modified to reproduce the ergicity of the process (6.1kcal/mole). Interpolation of the modified CI energies has been carried out by performing a Multi-Body expansion procedure. Diatomic components of the expansion have been fitted using a polynomial in the appropriate BO variable ($n_i = \exp\{-b_i(r_i - r_{ei})\}$). In a similar way, the three body term has been fitted polynomial of the sixth order in the three BO variables. The transition state height has been corrected by considering the estimate obtained from the more accurate CI values as an upper boundary and by making use of qualitative dynamical considerations.

To test the quality of the potential energy surface quasiclassical trajectories have been run. Values of reactive cross section (S_r) computed at the two collision energies of the experiment are $0.85 \pm 0.08 \mathring{A}^2$ and $9.34 + 0.26 \mathring{A}^2$ respectively. These results, although predicting reactivity at the lowest collision energies in agreement with experimental findings, lead to reactive cross section values lower than measured ones.

Comparison with experiments have been performed also for the calculated average product translational energy (80% and 67%) and for the computed average scattering angle (64 degrees). Both quantities are in excellent agreement with measured values.

A Method For Molecular Structure Determination Based Upon Simple Localized Bond Orbitals and Low-Order Perturbation Theory

18A

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ABSTRACT

A new, ab-initio method designed primarily to determine molecular structure has been developed. In this method, orbitals composed of orthonormalized linear combinations of atomic hybrids are employed and the energy is evaluated through either full second-order many-body perturbation theory (MBPT(2)) or MBPT(2) plus additional higher-order coupled Hartree-Fock corrections depending on basis set completeness. A distinguishing feature of the method is that external storage space is proportional to just n^2N^2 (where n is the number of occupied or virtual orbitals, whichever is smaller, and N is the number of basis functions) while the AO integrals need to be computed only once. Full or partial MINI1 and DZ geometry optimizations for methane, ethane, propane, cyclopropane and pentane have been carried out using our new method at the full MBPT(2) and MBPT(3) levels in addition to the standard SCF, SCF-MBPT(2) and SCF-SDQ-MBPT(4) methods. In addition, DZP optimizations using the same methods were carried out for all molecules except pentane. Geometry comparisons are presented along with methodological details and programming considerations.

18B

Full Configuration Interaction Calculations on the CRAY 2

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and

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Abstract

The large memory and vector capabilities of the CRAY 2 have permitted full configuration-interaction (FCI) calculations with expansions in excess of 25 million determinants. This has allowed us to calibrate approximations to the n-particle problem in one-particle basis sets of double-zeta plus polarization (DZP) quality or better. Once a correlation treatment is found that reproduces the FCI in a DZP quality basis, this treatment is then taken to the one-particle limit using very large generally contracted one-particle gaussian basis sets. The poster will include applications of this approach to the following problems: (1) determination of the singlet-triplet splitting in methylene; (2) determination of the ground state of Al_2; (3) determination of the electric dipole moment function of OH ($X^2\Pi$); and (4) determination of the dissociation energies of the NH, N_2, O_2 and F_2 molecules.

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18C

Theoretical Studies of Solvent Effects on the Decarboxylation of 2-Cyanoacetic Acid

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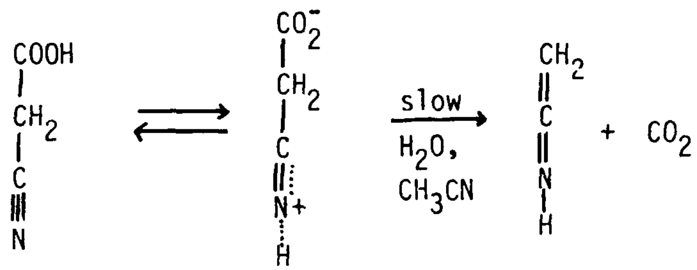
Solvent Effects on the decarboxylation of 2-cyanoacetic acid in H_2O and CH_3CN, (1), have been investigated MO theoretically using the AM1 method ;



(1)

Four regions around the substrate molecule were identified as the probable primary solvation shell. The water was found to solvate essentially by hydrogen-bonding while the acetonitrile had mainly polarization effect by solvation. Both solvate molecules stabilized the zwitterionic form so that caused elevation of activation barriers, the effect being markedly great with water. Solvation caused shortening of bond length and the increase in bond order for the C-C bond which is cleaving in the decarboxylation. The entropy term, $T\Delta S^{\neq}$, was found to become increasingly more favorable with the increase in the temperature for the reactions in solution. Lower barriers were found after the main activation barrier along the reaction coordinate due to the solvent reorganization.

18D

MULTI-REFERENCE CI DETERMINATION OF THE SINGLET-TRIPLET SEPARATION IN SILACYCLOBUTADIENE

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ABSTRACT

The geometries of the lowest singlet and triplet states of Silacyclobutadiene have been optimized at the MCSCF level. The energy separation was then determined from second-order CI calculations run at the optimum MCSCF structures. The vibrational frequencies were determined analytically from the MCSCF wavefunctions. The optimum structures and energy separation were found to be very different from earlier correlated calculations based on SCF structures.

The effect of increasing the size of the basis set on the energy separation and the optimum structures will be examined and the bonding will be compared to that found in calculations on Cyclobutadiene.

18B

Full Configuration Interaction Calculations on the CRAY 2

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and

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Abstract

The large memory and vector capabilities of the CRAY 2 have permitted full configuration-interaction (FCI) calculations with expansions in excess of 25 million determinants. This has allowed us to calibrate approximations to the n-particle problem in one-particle basis sets of double-zeta plus polarization (DZP) quality or better. Once a correlation treatment is found that reproduces the FCI in a DZP quality basis, this treatment is then taken to the one-particle limit using very large generally contracted one-particle gaussian basis sets. The poster will include applications of this approach to the following problems: (1) determination of the singlet-triplet splitting in methylene; (2) determination of the ground state of Al_2; (3) determination of the electric dipole moment function of OH ($X^2\Pi$); and (4) determination of the dissociation energies of the NH, N_2, O_2 and F_2 molecules.

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/8F

AN ATOMS-IN-MOLECULES ANALYSIS OF THE METAL-CARBONYL SYSTEMS $Mn_2(CO)_{10}$, $Fe_2(CO)_9$ AND $Co_2(CO)_8$.

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ABSTRACT Ab *initio* calculations have been performed on the systems $Mn_2(CO)_{10}$, $Fe_2(CO)_9$ and $Co_2(CO)_8$. Subsequently, the resulting wave functions and charge densities were analyzed using the quantum theory of atoms in molecules. The molecular structures of these systems were determined at the corresponding equilibrium geometries, only the manganese dimer was found to possess a metal-metal bond. Partitioning of the total energy into atomic contributions revealed that the stabilization which occurs during metal-carbon bond formation is attained chiefly within the physical boundaries of the carbon atoms. In the bridged systems the bridging carbon atoms were found to contribute the most to the overall stability. In all cases the oxygen atoms were destabilized as a result of metal-carbon bond formation.

The Laplacian of the charge distribution maps out regions of local charge concentration and depletion.[1] The "lumps and holes" in the valence shell of charge concentration (VSCC) of the metal atoms, features previously related to HOMO and LUMO respectively,[2] were found to agree with simple predictions using crystal field theory. Again, in the bridged systems the bridging carbon atoms interacted most strongly with the metal "d-orbitals", as evidenced by the pronounced holes in the VSCC of the metal atom which are directly in line with the corresponding metal-carbon bond path.

* This work was supported in part by a grant from the Petroleum Research Fund.

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18G

VIBRATIONAL SPECTROSCOPY OF DIATOMIC MOLECULES IN STATIC ELECTRIC FIELDS. AN *AB INITIO* STUDY OF HF

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For the specific case of the hydrogen fluoride molecule, a detailed determination of the vibrational effects on molecular electrical properties has been made for the lowest four vibrational states. Electrical properties at fixed H-F distances obtained from correlated and SCF-level *ab initio* correlated treatments were used along with an *ab initio* potential energy curve to describe the vibrating system. Using numerical vibrational wavefunctions, the electrical properties of the low-lying vibrational states were rigorously calculated by finite differences and these are compared with values obtained with certain approximate means. One and two-photon, dipole, and quadrupole absorption cross sections were calculated in the same manner. The extensive incorporation of electrical properties and the detailed treatment of the vibrational states provides certain fundamentally new information on (i) the role of vibrational motion in dipole and other types of transitions, and (ii) the effect of external electrical fields on vibrational effects.

18H

Theoretical Study on the Ground and Excited States of CuH

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Spectroscopical constants of the X $^1\Sigma^+$ ground state and several excited states of the CuH molecule have been determined using large AO basis sets. Extensive comparisons between single-reference SDCI, multi-reference SDCI, including a conventional MRCI with A_k-type selection and extrapolation (MRD-CI) and a direct externally contracted MRCI (CCI), and coupled pair functional methods (CPF and MCPF) are undertaken. The one-particle bases are thereby generated by either SCF- or CASSCF-calculations the active space varying from 4 to 12 orbitals in the latter. Inclusion of 3d - correlating configurations, exhibiting $d^2 \rightarrow d^{*2}$ excitations, both in the CASSCF and in the CI reference set is found to be important for the description of the eletron correlation in the (d^{10}) ground state of CuH on the CASSCF/MRCI level.

19A

Theoretical Studies of Molecular Ions : HNO^+, HNO_2^+ and OCN_2^+.

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Little is known experimentally about the gas-phase basicities or favoured protonation sites for nitrogen oxides. At the DZP SCF level of theory, the nitrogen and oxygen atoms in NO are almost equally basic, protonation being preferred at nitrogen by just 9 kJ mol^{-1}. However, oxygen in NO_2 is more basic than nitrogen by 286 kJ mol^{-1}. HNO^+, HON^+, HNO_2^+ and $HONO^+$ are all true minima on the potential energy surfaces. Correlation effects enhance nitrogen's basicity in both NO and NO_2, and produce substantial structural changes for HNO^+. Calculated proton affinities at 300 K are 586 kJ mol^{-1} for NO_2 and 531 kJ mol^{-1}, for NO. Both oxides are less basic than N_2O (measured PA 594 kJ mol^{-1}, calculated 607) and substantially less basic than water (697 kJ mol^{-1}).

Several different geometries for CO^+ approaching N_2 have been studied by SCF methods. OCN_2^+ is not linear in its ground state, with NNC and NCO angles of 180 and 131°. The DZP CISD binding energy is 98 kJ mol^{-1}, comparable to the experimental value for isoelectronic N_4^+, though that species is linear.

19B

Numerical Hartree-Fock Calculations on Transition Metal Diatomics

By

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ABSTRACT

Numerical single configuration and small multiconfiguration Hartree-Fock calculations have been performed on several transition metal diatomics, including diatomic titanium, chromium and copper. The results of these calculations will be presented and compared with previous basis set results for these molecules. Optimized basis sets derived from the numerical calculations will also be discussed. This work was supported in part by the National Aeronautics and Space Administration and by the National Science Foundation.

19C

Investigation of the Thermal Ring Opening of Bicyclobutane to Butadiene. Evidence for a Nonsynchronous Process

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The conrotatory ring opening of bicyclobutane to butadiene is predicted to occur in a two step process at the HF/3-21G level and involves 3-butenylidene as an intermediate. This prediction is in conflict with experimental results of labeling studies which show the reaction to be concerted. A reinvestigation of the reaction surface at the MP2/3-21G level leads to a concerted transition state for the conrotatory ring opening 43.6 kcal/mol above bicyclobutane ([MP4SDTQ/6-31G*]//MP2/3-21G + ZPC//3-21G), in good agreement with the known barrier for the thermal ring opening to butadiene which is 40.6 kcal/mol. In the MP2/3-21G transition state one C-C bond, while lengthening to 2.31A, is stabilized by partially π bond formation to the other adjacent carbon. The second breaking C-C bond is 1.62A in the transition state. The disrotatory ring opening (based on a C_2 transition state) has a predicted barrier of 97.0 kcal/mol at the [MP4SDQ/6-31G*] + ZPC//3-21G level of theory.

19D

KRAMERS DEGENERACY IN MOLECULES AND NONABELIAN ADIABATIC PHASE FACTORS*

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The phase factor experienced by an electronic wave function (or eigenfunction of any parameter-dependent hamiltonian) when the nuclear coordinates (or other parameters) traverse a closed path [1,2] has become a topic of considerable interest, not only in molecular quantum mechanics, but in such diverse fields as the theory of the quantum Hall effect [3], and elementary particle theory [4]. If there is a parameter-independent degeneracy, the phase factor is replaced by a unitary transformation mixing the degenerate states, and the set of such transformations forms a nonabelian group whose structure exactly parallels that of the gauge groups of present-day elementary particle theory. Kramers degeneracy is a perfect example of such parameter-independent degeneracy, and is thus capable of providing examples from the molecular world which exhibit gauge field behavior. A simple case which has been treated is that of an atom in a slowly rotating electric field [5], in which the component of angular momentum along the field can be changed by gauge field effects. Other situations in which analogous phenomena can arise are scattering processes in which amplitudes correspondiing to different paths, or differing in a permutation of identical nuclei, must be superimposed. We discuss these examples, and also consider the nonabelian generalization of the Berry solid-angle formula [2] for the phase factor. Coupling between Born-Oppenheimer levels provides a model for the coupling of different gauge fields. The study of this topic would appear to open up a wide variety of possibilities.

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AD-A195 528 AMERICAN CONFERENCE ON THEORETICAL CHEMISTRY HELD IN GULL LAKE MINNESOTA ON JULY 25-31 1987(U) MINNESOTA UNIV MINNEAPOLIS D G TRUHLER 1988 AFOSR-TR-88-0420 3/4

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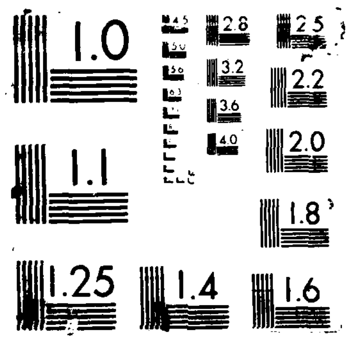
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19E

Ab initio Investigation of the Unimolecular Isomerization LiCN <=> LiNC

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There is much current theoretical interest in the relatively simple unimolecular isomerization LiCN <=> LiNC. From an *ab initio* electronic structure viewpoint, this system is interesting because of the sensitivity of both the low barrier and exothermicity to the level of theory used in calculating the potential energy surface[1]. From a reaction dynamics viewpoint, this system has a low barrier which allows for large-amplitude motion that must be adequately accounted for in the dynamical description of this system.

We have performed a large number of SCF and CI calculations on the groundstate potential energy surface of this triatomic system using a large gaussian-type-orbital basis set. The minimum energy path for this isomerization reaction has been obtained by minimizing the energy with respect to both the CN stretching coordinate and the Li-CN stretching coordinate for a number of values of the bending coordinate. The resulting potential energy surface has been incorporated in an appropriate Hamilitonian form[2] and the vibrational-rotational energy spectrum has been calculated. These results have been used to compare the present surface with previously calculated surfaces.

Finally, the rate constant for the LiCN <=> LiNC isomerization has been calculated employing two variants of the RRKM method[3].

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19F

ALL NUMERICAL HARTREE-FOCK ORBITALS FOR MOLECULES: THE APPROACH OF THE FUTURE?

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Numerical orbitals are an extremely accurate method of solving the Hartree-Fock equations. Rather than describing each molecular orbital as a finite expansion of simple basis functions, numerical orbitals describe them as an organized set of computed values. By eliminating the LCAO approximation, the unpredicable effects of basis set dependence on calculations which use SCF orbitals are thus avoided. Recently we proposed an algorithm which can compute numerical orbitals for general polyatomic systems. This approach is formulated in momentum space to avoid the numerous Coulomb singularities which exist in position space. In momentum space only one singularity exists at the origin and it can be numerically *removed*. In this poster we describe our algorithm, present results on a number of simple systems and speculate on the future use of numerical orbitals in quantum chemistry.

196

The Electronic Structure of H_6^+

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There has been great interest in recent years in the formation and stability of weakly bound hydrogen cluster ions. These systems have provided a fertile meeting ground for theory and experiment, as the smaller hydrogen clusters are amenable to accurate *ab-initio* calculations. In particular, the theoretical work of Schaefer's group[1] stimulated the first observations of the vibrational spectra of hydrogen cluster ions by Okumura, Yeh, and Lee,[2] and the calculations of Wright and Borkman[3] provided impetus for the first observation by Kirchner and Bowers[4] of the even-membered hydrogen cluster ions.

It is well known that odd-membered hydrogen cluster ions are formed from the addition of H_2 to H_n^+ (n odd),[5] but the analogous formation of even-membered hydrogen ion clusters by addition of H_2 to H_n^+ (n even) does not seem to have been observed. Indeed, it is only in the recent experments of Kirchner and Bowers[4] that the even-membered hydrogen ion clusters H_4^+, H_6^+, and H_8^+ have been positively identified. Especially interesting is their finding of large yields of H_6^+, in the near absence of H_4^+, and their suggestion that this is due to reaction of H_3^+ with H_3 Rydberg states rather than addition of H_2 to H_4^+. In an attempt to understand these important experimental results, we report in this paper the theoretical characterization of several stationary points on the H_6^+ potential energy surface.

Ab-initio calculations on H_6^+ were performed at the UHF and MP2 levels of theory using several basis sets of increasing accuracy. Using GAUSSIAN-82, optimized structures were found at the UHF/DZP level of theory for H_6^+ in C_s, D_{2h}, D_{2d}, and C_{2v} symmetries. Vibrational analysis indicated two stable structures, in C_s symmetry and in D_{2d} symmetry. The C_s structure is that found by Wright and Borkman;[3] the D_{2d} structure has not been previously reported. Additional calculations at the UHF/*4s1p*, UHF/*5s3p*, MP2/DZP and MP2/*4s1p* levels of theory were performed for the C_s and D_{2d} structures. The results of these calculations are summarised in Table I. It is especially interesting that the MP2 energies for the D_{2d} structure are lower than those for the C_s structure. Apparently electron correlation plays a crucial role in determining the ordering of these states.

We suggest, based on these calculations, that it is the D_{2d} structure that is observed by Kirchner and Bowers, as geometrically this structure seems more likely to be formed by simple association from H_3^+ and H_3^* collisions. In addition, our post-SCF energies indicate that the true ground state of H_6^+ is the D_{2d} structure, rather than the C_s structure.

TABLE I. H_6^+ calculated electronic energies in hartrees.

Level	UHF/DZP	UHF/*4s1p*	UHF/*5s3p*	MP2/DZP	MP2/*4s1p*
C_s	−2.935 336	−2.941 048	−2.945 928	−2.995 943	−3.003 311
D_{2d}	−2.930 948	−2.936 759	−2.939 781	−2.998 987	−3.006 855

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19H

Na_2 THEORETICAL SPECTROSCOPY

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The potential energy curves and related transition moment functions for more than 30 electronic states of Na_2 have been investigated using ab initio[1] and pseudopotential[2] valence CI techniques. Intershell correlation effects are accurately taken into account by means of core polarization potentials.[3] High accuracy is obtained for a variety of spectroscopic properties. Typical deviations from experimental values are: 50 cm^{-1} for dissociation and excitation energies, 1 cm^{-1} for vibrational frequencies, and 0.01 Å for equilibrium distances.
The data have been used to obtain theoretical spectra of Na_2: (i) Bound-free emission spectra in the singlet and triplet systems have been studied which establish conclusive electronic assignments of the violet bands of sodium,[4] and (ii) the entire absorption spectrum of Na_2 in the ultraviolet, visible, and near-infrared regimes has been calculated[5] using semi-classical Szudy-Baylis theory. In both cases, excellent agreement between theory and experiment is found.

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20A

New Bonding Concepts for Octahedrally Coordinated Molecules and Their Relevance to New High T_c Superconductors

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Abstract:

We will present novel bonding features in octahedrally coordinated molecules by considering the explicitly correlated wave functions as a coherent superposition of low symmetry generalized valence bond structures. Each of these symmetrically equivalent resonance structures can be described in a local valence bond framework which shows the tetrahedral nature of the bonding between atoms. This coherent superposition enhances the correlation and restores the molecular symmetry. The relevance of these new bonding concepts to the new high T_c perovskite like superconductors will be discussed.

208

1987 American Conference on Theoretical Chemistry

Polarization Propagator Calculations of Nuclear Spin-Spin Coupling Constants

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The nuclear spin-spin coupling constant can be calculated from the E=0 limit of the polarization propagator. We report calculations of all terms contributing to the coupling constants (J), namely the paramagnetic spin-orbit (PSO), the diamagnetic spin-orbit (DSO), the spin-dipolar (SD), and the Fermi-contact term (FC). Contrary to generally accepted expectations we find cases (N_2 and CO) where the PSO term instead the FC term give the dominant contribution to J.

We also discuss results of propagator calculations of coupling constants based on a coupled cluster reference state.

The applications of the method include results for the HF, CO, N_2, CH^+, C_2H_2, and H_2O molecules.

20C

Vibration-Induced Electron Detachment in Acetaldehyde Enolate Anion

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An *ab initio* theoretical simulation of the rate of electron detachment resulting from the torsional vibrational motion in the acetaldehyde enolate anion will be discussed. This calculation is aimed at helping interpret recent Ion Cyclotron Resonance experiments in which electron loss is seen to occur following vibrational excitation. Also involved in the calculation is a full geometry optimization of the anion along the vibrational coordinate.

20D

An MCSCF Study of the Structures and Vibrational Frequencies of the Lowest Excited States of Benzene

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The molecular structures and vibrational frequencies are evaluated for the ground and low-lying excited states of benzene by using *ab initio* MCSCF method. In the calculation, minimal and split valence type basis sets are used, and all the electron configurations in six π orbitals are considered in the MCSCF procedure. The equilibrium structure in the lowest excited singlet state $^1B_{2u}$ has D_{6h} symmetry, and the bond lengths of C-C and C-H are calculated to be 1.450 Å and 1.082 Å, respectively. The ordering of the vibrational frequencies agrees very well with experimental results for both $^1B_{2u}$ state and the $^1A_{1g}$ state. The vibrational modes are well reproduced especially for the frequency shifts in B_{2u} mode (ν_{14} and ν_{15}), caused by the electronic excitation from the ground state to the $^1B_{2u}$ state.

The potential energy surface in the lowest excited triplet state, $^3B_{1u}$, suggests that the structure of benzene does not maintain D_{6h} symmetry and distorts to D_{2h} symmetry. The vibrational analysis gives the degenerate imaginary frequency 1003 i cm^{-1} for E_{2g} mode (ν_8) at the D_{6h} geometry (R_{CC} = 1.443, R_{CH} = 1.081 Å). The equilibrium structure is calculated to be quinoidal form, and the anti-quinoidal form is found to be the transition state for the pseudo rotation of benzene ring.

20E

The Methoxy Radical: Decomposition Versus Isomerization

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The methoxy radical is a transient species felt to be important both in atmospheric chemistry and in hydrocarbon combustion. Two possible unimolecular pathways open to methoxy are decomposition yielding formaldehyde and a hydrogen atom and hydrogen transfer yielding the hydroxymethyl radical. We present multiconfiguration SCF and multireference CI calculations of the relevant features of the potential energy surface to address this competition. Stationary point structures are fully optimized at the MCSCF level using a variety of basis sets up to triple zeta plus polarization quality. Our results stand in contrast to previous theoretical treatments.

20F

MOLECULAR APPLICATION OF MULTIREFERENCE COUPLED-CLUSTER METHODS TO EXCITATION ENERGIES

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Direct excitation energies for several molecules are reported using a recent development of a linked, multireference coupled cluster formalism based on a general, incomplete model space. The reference space consists of a set of particle-hole excited determinants built from all of the set of active particles and holes in the model space. The model space is incomplete. Numerical applications are reported for several molecules and compared with other available results as well as experiment.

+Guggenheim Fellow.

206

Comparisons and Peculiarities of Geometry Optimization

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The geometries of isopropanol and axial- and equatorial-cyclohexanol have been optimized using two different molecular mechanics procedures and using the standard Hartree-Fock method. The results are compared and analyzed.

Several chainlengths of polyacetylene molecules (including radical solitons) have been studied using Hartree-Fock, unrestricted Hartree-Fock, perturbation, and valence-bond methods. The unrestricted Hartree-Fock method introduces incorrect spin components that result in poor predictions for geometrical parameters. The situation is not remedied by the standard second order perturbation corrections (MP2).

20H

Near Hartree–Fock quality GTO basis sets for the second–row and third-row atoms

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Abstract

Energy optimized, near Hartree–Fock quality Gaussian basis sets are presented for the ground states of the second–row and third–row atoms and for Na (^2P), Na^+, Na^-, Mg (^3P), P^-, S^-, Cl^-, Cr (^7S), Ni (^3D) and Cu (^2D). The second–row basis sets range in size from (17s12p) to (20s15p) and the third–row basis sets range in size (20s12p8d) to (23s16p12d). In addition, for the second-row atoms optimized supplementary functions are given for the ground state basis sets to describe the negative ions, and the excited Na (^2P) and Mg (^3P) atomic states. For the third–row atoms optimized supplementary functions are given to the s^2d^n basis sets to describe the s^1d^{n+1} and d^{n+2} atomic states. The ratios of successive orbital exponents describing the inner part of the 1s and 2p orbitals are found to be nearly independent of both nuclear charge and basis set size. This provides a method of obtaining good starting guesses for other basis set optimizations. All of the basis sets are at least TZ in the valence shell and are balanced, that is, equal accuracy in each shell is achieved.

21A

Theoretical Study of the Structures and Stabilities of Molecular Complexes I: Complexes of SO_2

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Sulfur dioxide is one of the most prevalent atmospheric pollutants. It originates from both natural and anthropogenic activities. Its omnipresence in the atmosphere from terresterial and ocean sources provides opportunity for the formation of molecular complexes with a large variety of molecules and radicals. Some of these may serve as the percursors to aerosol formation or aggregates which subsequently undergo gas-to-particle conversion.

This report describes the results of ab initio calculations used to examine the structure and stability of several molecular complexes of SO_2 with nitrogen-containing molecules. The structures for each complex are first optimized at the Hartree-Fock level using basis sets of double zeta quality. For those complexes which appear to be stable at this level of approximation, additional studies were undertaken. Of particular interest is the effect of basis set composition on the predicted complex stability (after taking account of basis set superposition error). Finally the results from the H-F level calculations are compared with limited post-SCF results.

Supported in part by Atmospheric Chemistry Division, NSF.

21B

CONSISTENT GENERALIZATION OF MOLLER-PLESSET PERTURBATION THEORY TO ARBITRARY OPEN-SHELL AND MC-SCF REFERENCE STATES

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Many-body perturbation theory (MBPT) is the most efficient method for treating dynamical electron correlation . It derives its efficiency from the consistent neglect of higher order contributions, obviating the iterative loops characteristic of variational CI and coupled cluster techniques.

The major weaknesses of MBPT are (1) the dependence on the partitioning of the Hamiltonian, and (2) its inability to treat near-degenerate correlation. For closed-shell systems, the Møller-Plesset (MP) partitioning was found the best empirically. The latter can be naturally generalized for open-shell systems described by UHF reference functions. UHF-MPPT has, however, significant disadvantages. The UHF wave function may be far from a pure spin state, and perturbation theory cures this very inefficiently. Computational effort in UHF-MPPT is high. An MP type partitioning for restricted open shell wave functions has been suggested by Hubac and Carsky but it is not a clear analogue of the MP partitioning. For the near-degenerate case, one should start with a small MC-SCF wave function which takes care of the degeneracy. This results in a closed shell-like treatment, quite different from quasi-degenerate perturbation theory. One has, however, to define H_o in the MC-SCF case consistently with the closed-shell and UHF case.

Following our work on MP perturbation theory with localized orbitals[1,2], we propose such a generalization of the MP partitioning which is applicable to arbitrary reference states. The key point in which our proposal differs from previous attempts of this kind is that we do not requite that the orbitals be eigenfunctions of the zeroth-order Fock-like operator. Our implementation of localized perturbation theory[1,2] has shown that the efficiency of MBPT does not suffer appreciably if the orbitals are not eigenfunctions of H_o.

Our zeroth-order Hamiltonian is given by

$$H_o = PFP + QFQ; \quad F = \Sigma\, f(i); \quad P = |\Psi\rangle\langle\Psi|; \quad Q = 1 - P.$$

The one-electron Fock operator f is defined as $f = h + J - K$, where J is the Coulomb operator built from the total reference charge density, and K is the corresponding exchange operator. To improve efficiency and to make the method more similar to the closed-shell case, the perturbational wave function is sought in the internally contracted form, as originally suggested by Werner and Meyer for MC-CI. Our initial implementation will be described and examples will be presented.

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21C

ELECTRONIC STRUCTURES AND CHEMICAL REACTIONS OF SMALL SILICON CLUSTER IONS

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Accurate *ab initio* quantum chemical calculations have been performed to investigate the nature of the structures and energies of the positive ions of $Si_2 - Si_6$. The effects of polarization functions and electron correlation have been included in these calculations. The ground state geometries of the ions are found to be very similar to those of the corresponding neutral systems. In all cases the electron which is removed on ionization of the neutral cluster comes from an orbital which is principally non-bonding in character thus resulting in fairly small structural modifications. Ionization potentials have been computed for all the clusters and compared with the results of recent experimental measurements. The relative stabilities of ionic silicon clusters are discussed.

The chemical reactivity of ionic silicon clusters with silane (SiH_4) has also been investigated carefully. These studies yield not only the energies of various reaction products but also yield detailed information about the transition states and the associated barriers for the different reaction channels. The reaction mechanisms show clearly that small silicon cluster ions react with silane to yield larger clusters containing some hydrogen atoms. For example, the chain reactions of Si^+ with silane yield consecutively $Si_2H_2^+$, $Si_3H_4^+$, $Si_4H_6^+$ and $Si_5H_{10}^+$. By eliminating reaction channels involving high barriers, it has been possible to identify specific isomeric product structures in most cases. The product distributions and implications for isotope exchange reactions are compared with the results of recent experiments.

21D

INTERNAL ROTATION OF THE C—OH BOND IN NEUTRAL GLYCINE

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Previous ab-initio SCF studies of glycine in its neutral form describe three local minima of C_s symmetry (**I**, **II**, and **III**) with energies $E_I < E_{II} \approx E_{III}$ (**II** is stabilized by an intramolecular N···HO interaction). [1-4]

```
                                   O
           OH                     //                          O
          /                  H2C—C                           //
   H2C—C                      /     \                   H2C—C
    /    \\                H2N       O                   /     \
  NH2     O                         /                  NH2     O—H
                                   H

       I                        II                         III
```

While **I** and **III** and the internal rotations of the C—C and the N—C bond have received a constant interest over several years, **II** has been given only minor attention. [4-8]
This work presents a 4-21G [9] ab-initio SCF study of the internal rotation of the C—OH bond, i. e. the energy profile of **II** → **I** and **II** → **III** .

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21E

Anisotropic Atomic Densities from X-Ray Diffraction Analysis

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The diffraction of X-rays by electrons in crystals furnishes one of the most powerful means of determining molecular structures in all areas of chemistry. For more than half a century the experimentally attainable accuracy was however only sufficient for determining essentially geometric type of molecular information and, at that stage of the development, it proved quite adequate to base the analyses on theoretical models in which the atoms are taken to be spherically symmetric scattering centers. More recently experimental techniques have been improved to the point where it has become possible to determine finer details of electron densities, details which are believed to embody information relevant to chemical bonding. In this context, it has become apparent that the electron densities which are responsible for the observed X-ray data differ noticeably from densities that can be generated by means of spherical atomic contributions. Such observations are not surprising to quantum chemists. Indeed, in a recent in-depth study of the characteristics of theoretical electron densities this group documented the very substantial deviations from spherical symmetry that can occur around the atomic nuclei in a molecule.

In view of these results an analysis of X-ray diffraction which is based on contributions from *anisotropic* atomic scattering densities has been developed. The atomic electron densities are expanded in terms of the minimal-basis-set self-consistent-field orbitals of the free atoms. Instead of a single form factor each atom has now a form factor *matrix*. Its elements are in general complex and no longer spherically symmetric. The interpretation of the atomic density matrices yields hybrid atomic orbitals and associated occupation numbers which characterize the atomic bonding situation.

Since a better electron density model should allow for a more accurate representation of the experimental scattering, one would hope for a more precise determination of the atomic positions and physically more realistic thermal parameters. More interestingly, consistent anisotropic atomic scattering contributions should provide a more incisive source of information regarding bonding interactions than the mere comparison of interatomic distances. Moreover, difference densities calculated with respect to the anisotropic atomic densities should prove more illuminating than those obtained with respect to spherical atomic densities.

Acknowledgment

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21F

AB INITIO SCF APPROACH TO MOLECULAR SOLIDS UNDER PRESSURE: MOLECULAR ORBITAL EFFECTIVE POTENTIALS*

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Traditional ab initio methods for the study of molecular solids have involved several approaches: simulation with finite clusters; the use of pair potentials; density-functional approaches; and $\vec{k}$ vector delocalization schemes. All of these methods have proved successful for the study of molecular solids at ambient pressure, but all have limitations for their application at high pressures where many-body effects become important, and where the potential exists for the occurrance of pressure-driven chemical reaction.

We have developed an ab initio self-consistent-field approach for the study of molecular crystals and clusters which explicitely contains all many-body interactions, takes maximum advantage of crystal periodicity, and maintains the chemical "identity" of the crystal components. In so doing, the method provides for a complete partitioning of the total crystal energy. Molecular reactions and interactions can then be studied directly, with all many-body interactions included. Furthermore, the approach is completely general, allowing for use of semi-empirical applications as well as exact applications, as desired.

In this paper, we will discuss the development of molecular orbital effective potentials as useful and efficient means of reducing computational complexity. Several approaches and their application to simple systems will be considered.

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216

Ab *initio investigations on local anesthetics and antiarrhythmics*

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Different investigations show that the effect of local anesthetics is a reversible blockage of nerve conduction, although the molecular mechanism is still not clearly understood. Most of the clinically used local anesthetics can be characterized by the general scheme: aromatic part - polar group - connecting chain - amino group. Of the chemically different groups of local anesthetics the esters and the anilides are the most frequently used clinically. It is supposed that also local anesthetic antiarrhythmics can interact with biological receptor in a similar manner.

This work reports on the results of the authors' ab initio SCF MO investigations of the local anesthetics and antiarrhythmics of the ester, anilide and carbamate types. The electrostatic molecular potential contour maps were evaluated for aromatic parts of both active and inactive derivatives of those types of drugs.

Because the main constituents of cell membranes are lipids and proteins, our further ab initio SCF MO studies were concerned with interaction of polar groups of local anesthetics with possible associative sites of nerve membrane. Aniline, formanilide and trimethylamine represent possible associative sites of the local anesthetics procaine and lidocaine. Dimethylphosphate monoanion, o-phosphate monoanion and acetamide represent associative sites of the membrane. The results of our calculations are discussed in terms of present theories of molecular mechanism of local anesthesia.

21H

MOLECULAR QUANTUM MONTE CARLO: NEW DIRECTIONS AND NEW RESULTS

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Molecular quantum Monte Carlo (QMC) is a procedure for solving the Schrödinger equation using methods of statistical mechanics. The essence of the approach is the simulation of an appropriate random process. The formal similarity of the Schrödinger equation to a diffusion equation allows one to calculate quantum expectation values as Monte Carlo averages over random walks. Using a fixed-node, short-time implementation of QMC, we have previously obtained highly accurate correlation energies for a number of atoms and small molecules, as well as numerous chemical properties in the ground and excited states, such as the singlet-triplet splitting in methylene, the reaction barrier height for $H + H_2$ exchange, the electron affinity of fluorine, excited-state energies of He and H_2, "analytic" Monte Carlo energy derivatives, and a number of other molecular properties. This work has shown that QMC is a powerful alternative approach to *ab initio* molecular calculations. We are currently developing and using a new QMC approach to compute excited states together with the ground state, in a single calculation. In this approach, excited state energies are all upper bounds to their true energies. In another direction, we are now treating molecular properties for which the usual QMC "mixed averages" are not appropriate, such as moments of the charge distribution. Additionally, we are developing and testing algorithms for computing transition moments. In the direction of improved efficiency, we are currently working on improving the importance-sampling function (which can significantly reduce the amount of computing required), on improving the Green's function (to more efficiently move through configuration space), and on correlated sampling techniques. Another direction that has proved exciting involves the use of effective-core potentials in the QMC framework (see poster by Hammond *et. al.*) to reach larger systems, and to avoid the problems encountered at large Z. Finally, we are seeking energies on smaller scales, such as binding energies in clusters.

We acknowledge support from the Office of Naval Research and the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under contract No. DE-AC03-76SF00098.

22A

Ab Initio Calculations On High Spin States of CO and CH

by

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ABSTRACT

As part of our current interest in potential novel energy storage devices we have investigated several high spin states of CO and CH. The results of our calculations on the $^5\Sigma^+$ and $^5\Pi$ states of CO and the $^4\Sigma^-$ state of CH will be discussed. The possibilities for spin-orbit interactions involving these high-spin states will also be considered.

22B

Quantum Mechanical Calculations on Polyimide Model Compounds

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ABSTRACT

X-Ray and ultraviolet photoemission studies are important experimental tools used in the surface characterization of polyimides which are used in electronics packaging. One important adjunct of this work involves molecular orbital calculations of the valence and core electronic level positions that are responsible for the observed spectra. This research will focus on obtaining calculated C1s, N1s, and O1s core levels and determining the amount of relaxation energy associated final hole state for each of these ionization processes. Another aspect of this work involves the determination of the nature of shake-up processes accompanying XPS events in polyimides.

The calculations involve using the MELD program in obtaining energies, charges and other properties such as relative intensities of C1s peaks for model compounds of the polyimides.

22C

RELIABLE DIFFUSION MONTE CARLO: APPLICATIONS TO H_2, LiH, AND H_2O*

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Diffusion Monte Carlo (DMC) is a random walk computational method for solving the ground-state Schroedinger equation for atoms and molecules. One obtains a biased simulated energy which, when plotted versus the time step and extrapolated to zero, yields an upper bound to the exact energy. The curve is very sensitive to the values of the parameters which appear in the trial function which guides the simulation. Unless the nuclear regions of configuration space are carefully sampled, the simulated energy versus time step curve is steep and extrapolation unreliable: the extrapolated intercepts are highly dependent on the assumed time step dependence of the simulated energy (model bias). In the case of water for an unoptimized trail function consisting of a double-ζ quality SCF with Jastrow correlation function, the model bias is approximately 0.07 a.u., which is 19 % of the correlation energy.

We report a simple and efficient technique to improve the guiding functions used in DMC, substancially reducing the time step dependent bias of the simulated energy. For the titled molecules we observe a dramatic improvement in both the accuracy and percision of DMC energy estimates,with a corresponding significant improvement in the reliability of the extrapolated energy.

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22D

HYDROGEN BONDING AND PROTON TRANSFERS INVOLVING TRIPLY BONDED ATOMS. HC≡CH AND HC≡N

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The formation of the H-bonded complexes $(HCCH{\cdot\cdot}CCH)^-$, $(NCH{\cdot\cdot}CN)^-$, $(CNH{\cdot\cdot}NC)^-$, $(NCH{\cdot\cdot}NC)^-$, and $(CNH{\cdot\cdot}CN)^-$ and the subsequent proton transfers taking place within them are studied by ab initio methods. When all H-bonds are constrained to the same length, the proton transfer barrier diminishes as the acceptor group becomes more basic. Hence, the "intrinsic" barrier for proton transfer between C atoms is lower than for internitrogen transfer. However, greater acidity of the proton donor group leads to a stronger and hence shorter H-bond in which the proton needs to traverse a smaller distance from donor to acceptor. Consequently, when the length of the H-bond is freed of external restraint, the dominant factor controlling the height of the transfer barrier switches from the acceptor to the donor group. While the full potential energy surface characterizing proton transfer between C atoms contains a pair of equivalent minima separated by an energy barrier, internitrogen transfer occurs in the absence of a barrier. Only one minimum, corresponding to $(NCH{\cdot\cdot}NC)^-$, is present in the potential of the asymmetric system. These principles explain the previously observed difference in proton transfer behavior between C-acids and normal acids containing N and O atoms.

22E

Pi Bonding by Main Group Elements

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The strengths of all possible pi bonds between the main group elements C, N, O, Si, P, and S are presented. The pi bond strengths are estimated in two ways: from the *cis-trans* isomerization barriers, computed by SOCI/6-31G(d) wavefunctions based on MCSCF/3-21G(d) transition states, and by hydrogenation thermochemical cycles, using fourth order perturbation theory and triple zeta plus polarization bases. Combination of the very few experimental values, with both sets of theoretical values, gives the following recommended pi bond energies: C=C, 65; Si=C, 38; Si=Si, 25; N=N, 60; P=N, 44; P=P, 34; C=N, 63; Si=N, 36; C=P, 43; Si=P, 29; C=O, 77; Si=O, 50; C=S, 52; Si=S, 50; N=O, 62; P=O, 53; N=S, 42; and P=S, 40 kcal/mol. An analysis of these pi bond strengths shows that the ability of these elements to form strong pi bonds is in the order O > N = C >> S > P > Si.

Besides participating in localized double bonds, main group elements can belong to aromatic rings. The ability of the second, third, fourth, and fifth row main group elements in Groups 14, 15, and 16 to participate in single heteroatom five and six member aromatic rings is presented. The resonance stabilization energy of these rings is computed by isodesmic and superhomodesmic bond separation reactions at the RHF/3-21G* level.

22F

The Theory for the Analytic Evaluation of Energy Gradients for the Single and Double Excitation Coupled Cluster (CCSD) Wavefunction

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ABSTRACT

The theory for the analytic evaluation of energy gradients for coupled cluster (CC) wavefunctions is presented. In particular, explicit expressions for the analytic energy gradient of the CC singles and doubles (CCSD) wavefunction for a closed-shell restricted Hartree-Fock reference determinant are presented and shown to scale as N^6 where N is the total number of atomic basis functions for the molecular system. Thus analytic CCSD gradients are found to be of the same magnitude in computational cost as is the evaluation of analytic gradients for the configuration interaction singles and doubles (CISD) wavefunction. Unlike the gradient of the CISD energy (a variational method), one must evaluate the contribution from the change in electronic energy with respect to the configuration coefficients, $\frac{\partial E}{\partial \underline{t}}$, when considering the coupled cluster gradient; thus, the first-order coupled perturbed CC equations must be solved. We show that, in order to formulate these CP-CCSD equations such that they scale as N^6, an iterative approach must be employed because it has been found that direct construction of the CP-CCSD A matrix scales as N^7.

22G

Abstract for the 1987 American Conference on Theoretical Chemistry, Gull Lake, Minnesota, 27-31 July 1987.

"Generalised Valence Bond Theory and ^{13}C Chemical Shifts"

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ABSTRACT

Over the past five years ^{13}C nuclear magnetic resonance (nmr) spectroscopy has impacted tremendously on the determination of molecular structures. This recent rapid growth underscores the need for a theoretical framework in which chemical shifts of ^{13}C can be predicted and interpreted by ascertaining the magnetic shielding tensor and determining the relationship between the tensor and the molecular electronic structure. Treatment of this problem is grounded in finding an origin for the vector potential that describes the magnetic field. At the ab initio SCF level, this problem can be resolved through modification of the orbitals of the wavefunction by gauge functions, which lead to shifts of the gauge origin. While several investigators have incorporated this modification, the methods in which it has been incorporated limit the interpretation of the results or are limited in their appplicability. The broad-based usefulness of generalized valence bond theory overcomes these limitations, resulting in amenability to interpretation and application to a wide variety of molecules.

This work was supported by the NSF.

22H

AB INITIO CALCULATIONS ON MEDIUM-SIZED HYDROCARBONS

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For the past several years we have been applying ab initio molecular orbital theory to hydrocarbons containing from seven to twenty carbon atoms. These calculations were performed with our own programs, which are highly optimized for the IBM SYSTEM/370 instruction set. The latest versions exploit the vector facility of the 3090 machines.

Systems most recently studied are the (n)-prismanes, with n = 3 to 9. We report the results of SCF calculations at the 6-31G* level for these molecules and 6-31G*/RMP2 calculations for the smaller prismanes. Comparisons with semiempirical and molecular mechanics calculations are made.

We have also performed ab initio calculations on some benzenoid and non-benzenoid hydrocarbons, compounds which have been little studied by these methods. Preliminary results on some molecules are reported.

23A

Representation of delocalized states using correlated valence bond wave functions

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Representation of excited/ion states within mean-field theories (e.g. Hartree-Fock) is conveniently described as excitations/removals of single electrons in delocalized orbitals. This produces wave functions of the proper symmetry as these orbitals have the full symmetry of the system. Ground states are more conveniently described in an explicitly correlated approach such as the generalized valence bond method, in which the spatially localized correlated orbitals that variationally result are readily and uniquely interpreted in terms of bond pairs and lone pairs. Recent results using these correlated wave functions indicate that carbon, for example, exhibits approximate tetrahedral hybridization in many bonding environments (including benzene) and as a consequence none of the correlated orbitals have the symmetry of the system. We present a description of delocalized ion states in which the electron is removed from a local correlated orbital and this hole is allowed to hop from bond to bond, so that a total wave function is obtained as a linear combination of many-electron valence bond terms with local holes. The relative phase of the hole as it hops determines the symmetry of the wave function. This prescription leads to quantities (matrix elements) that can be transfered between systems in order to calculate photoemission spectra. Calculations on molecular systems such as N_2 and CO_2 illustrate the utility of such an approach and demonstrate the importance of correlation effects.

The cyclic structure, 1, corresponds to a shallow minimum on the HF/6-31G*//6-31G* hypersurface, 23.2 kcal/mol below the energy of the separated fragments, $C_2H_2O^{+\cdot}$ and C_2H_4. The α-cleavage for ring opening of 1 requires an activation energy of 3.4 kcal/mol only, leading to the 1-oxo-tetramethylen radical cation 2 which is 6.6 kcal/mol more stable than (1). In fact, ESR studies indicate that oxidation of 1 generates irreversibly 2 [7]. 2 may dissociate continuously endothermic via a ß-c-c-cleavage. The alternative ring-opening of 1 via cleavage of the ß-bond leads to the 2-oxo-tetramethylene radical cation (3) being 29.3 kcal/mol less stable than (1) and 5.9 kcal/mol above the cycloreversion products. As a consequence, this route will not any longer be considered for both the fragmentation of $C_4H_6O^{+\cdot}$ to $C_2H_2O^{+\cdot}/C_2H_4$ and the reverse reaction. With regard to the cycloaddition we thus conclude that the centre of preferential attack in ketene$^{+\cdot}$ is the methylene group rather than the carbonyl carbon atom. In terms of the FMO model, this can be attributed to a dominant orbital interaction between the SOMO of ketene$^{+\cdot}$ and the HOMO of ethylene representing 3-electron-2-orbital interaction (Fig. 2). In contrast, ethylene approaches neutral ketene towards the central carbon before rotating the methylene group for ring closure [8]. This approach is governed by a 2-electron-2-orbital-HOMO(ethylene)-LUMO(ketene)-interaction.

Other $C_4H_6O^{+\cdot}$ isomers and the barrier of their interconversion based on an improved theoretical level (MP3/6-31G**//6-31G* + ZPVE) will be presented at the conference together with the analysis of alternative modes for the reaction $C_2H_2O^{+\cdot} + C_2H_4 \longrightarrow C_4H_6O^{+\cdot}$. The experimental results by Gross et al., in particular the labeling experiments, will be discussed in detail in the light of our theoretical findings.

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Fig. 1

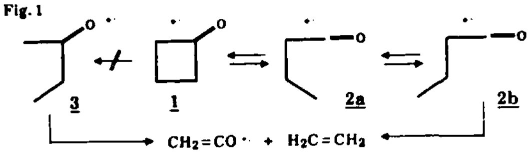
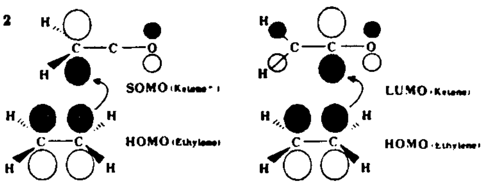


Fig. 2



3-Electron-2-orbital-interaction   2-Electron-2-orbital-interaction

Are Core Excitations of Symmetrical Molecules of Localized and of Single Particle Nature ?

233

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For benzene and its derivatives one expects three groups of core electron excitations from C1s to the three empty π^* MOs.

However, C1s$\rightarrow 1\pi^*, 2\pi^*$ gives rise to a single strong feature only in the experimental spectra. The symmetry-restricted MO-SCF model predicts the excitation energies too high (as known from diatomics), in addition, the level pattern is incorectly predicted for symmetrical molecules with several equivalent cores. Broken-symmetry SCF yields a reasonable energy pattern. Symmetry-adapted MCSCF yields both reasonable energies and wave-functions.

On the other hand, C1s$\rightarrow 3\pi^*$ gives rise to several weak transitions. According to MCSCF calculations these are of multi-particle nature, which cannot be obtained with any single particle approach (broken-symmetry SCF, g-Hartree, $X\alpha$, semiempirical MO).

Arguments in the literature concerning the physical localization of a hole on several equivalent cores are critically reviewed. In light diatomic (or heavy polyatomic) molecules the stationary core excited states (neglecting Auger decay) are delocalized (or localized, resp.). The character of the actually created state, however, depends on the excitation process. In the optical limit (XUV or low angle EEL) the created states are delocalized. An experiment to test these statements is suggested in detail.

23C

Optimizing Orbitals for the CCSD wavefunction

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The purpose of this work is to make the CCSD energy stationary with respect to molecular orbital (MO) variations in the reference configuration. To achieve this goal, we have use the idea sketched by Rice and coworkers (J. Chem. Phys. 85, 963 (1986)), where the Z vector, solution of the CPHF equations is used to rotate the MOs. A new energy energy and gradient calculation is carried out with these non-SCF orbitals in order to obtain a new Z vector. The process is repeated until the orbitals are optimized (Z = 0), ie the contribution to the analytic CCSD energy gradient coming from orbital relaxation (CPHF) is zero. In order to accelerate the process extrapolation techniques are used.

The wavefunction thus obtained is the analogue of the MCSCF wavefunction constructed from all single + double + CCSD higher excitations from a single reference, but with configuration coefficients fixed by the CCSD procedure.

Results for several molecules are presented.

HIGH QUALITY CH_2 POTENTIAL ENERGY SURFACES

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Multireference CI potential energy surfaces for the $^3B_1$ and $^1A_1$ states of CH_2 are being computed using a very large basis set and a complete valence space reference set. These surfaces will allow the calculation of accurate minimum-energy geometries, vibrational energy levels, and the zero-point vibrational contributions to the singlet-triplet splitting. They should also facilitate improved accuracy in the determination of the singlet-triplet splitting from the experimental laser magnetic resonance data.[1]

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23E

Exchange Interactions in Nickel Surfaces and Crystals

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Previously, our ab initio results on the "d electron rich" transition metal dimers[1] have revealed that the d electrons localize around the nuclei, and therefore hardly participate in the bond formation. The various exchange couplings of the d electrons, however, give rise to numerous low-lying electronic states. The detailed results of the ab initio calculations on the dimers form the background for the development of a new model that in particular focus on the magnetic properties of extended "d electron rich" transition metal systems. Results will be presented for a Nickel crystal as well as for Nickel surfaces of various symmetries.

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Poster Abstract

-3F

Spin-orbit interaction in the excited states of the dihalogen ions F_2^+, Cl_2^+ and Br_2^+

by

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In recent years a considerable body of experimental data has been accumulated on the low-lying excited states of the dihalogen ions F_2^+, Cl_2^+ and Br_2^+ . In particular the $^2\Pi_u$ state has been studied with a variety of techniques, including photo-electron spectroscopy, laser-induced fluorescence, low rotational temperature supersonic beam experiments etc. In all three molecules certain anomalies have shown up in the spectra, albeit of a rather different nature in the respective systems. In F_2^+ only one vibrational state shows anomalous intensity in Cl_2^+ the vibrational structure of the two spin-orbit components is heavily perturbed and finally in Br_2^+ both spin-orbit components show a regular vibrational structure but at rather different vibrational frequencies .

In order to investigate these effects relativistic Hartree-Fock-Slater calculations have been performed on Br_2^+ to see if the difference in vibrational frequencies between the two spin-orbit components can already be understood on the one-electron level. It turns out that the spin-orbit constant depends only weakly on the internuclear distance and consequently this dependence cannot explain the experimental facts.There are, however, several states arising from another configuration that cross the $^2\Pi_u$ state in the relevant range of internuclear distance. These states can in principle interact through the spin-orbit operator with the components of the $^2\Pi_u$ state. Since, however, the crossing states derive to a first approximation from a configuration that differs in only one orbital from the main configuration of $^2\Pi_u$ and since the most important part of the spin-orbit operator is a one-elctron operator, such an interaction would be too small to account for the experiments.

If one takes into account CI, however, it turns out that mainly due to the localization of the π-hole there is a substantial amount of configuration mixing both in the $^2\Pi_u$ and in the crossing states, such that important components of both states only differ in one orbital. Consequently there is a considerable spin-orbit interaction leading to a strongly avoided crossing. Since different states interact with the two spin-orbit components of the $^2\Pi_u$ and cross the $^2\Pi_u$ at different internuclear distances, the states that obtain after atking into account the avoided crossing show very different vibrational frequencies, that are now in good agreement with experiment.

It is also shown that the anomalies in the spectra of F_2^+ and Cl_2^+ can be explained by the same mechanism, if one realizes that in these molecules the spin-orbit interaction is of the same order of magnitude as the vibrational quanta, so that one cannot incorporate the spin-orbit interaction in the electronic Hamiltonian, but has to be treated after the vibrational proble n is solved, leading to a perturbed vibrational spectrum.

235

COMPARISON OF MBPT AND COUPLED-CLUSTER METHODS WITH MR-CI. POTENTIAL CURVE FOR THE C-H DISSOCIATION IN METHANE.*

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Many body perturbation theory (MBPT) and coupled-cluster (CC) methods based upon a restricted (RHF) and unrestricted (UHF) Hartree-Fock reference function are compared with recent MR-CISD results for the C-H bond dissociation in methane. Since UHF based correlated methods are not spin eigenfunctions, spin multiplicity formulae for the correlated many body perturbation theory and Coupled Cluster are applied to evaluate the multiplicity along the potential energy curve.

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+Guggenheim Fellow.

23H

EFFECTIVE HAMILTONIANS FOR MANY-ELECTRON SYSTEMS

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During the past decade, methods have been proposed and implemented which allow the removal of atomic core electrons from quantum mechanical calculations on molecules containing heavy atoms [W.J.Stevens and M.Krauss, Ann. Rev. Phys. Chem. 35, 357(1984)]. A popular technique involves the use of an effective core potential (ECP) to replace the core-valence term in the valence Hamiltonian:

$$H_{val}^{eff} = H_{val} + V_{core}^{eff}$$

The ECP represent the coulombic, exchange, and orthogonality interactions between the valence electrons and the core. They may be derived from atomic Hartree-Fock or Dirac-Fock wavefunctions by any of several methods, including direct inversion of a Hartree-Fock equation [L.R.Kahn, P.Baybutt, and D.G.Truhlar, J. Chem. Phys. 65,3826(1976)], or direct optimization of parameters [W.J.Stevens, H.Basch, and M.Krauss, J. Chem. Phys. 81,6027(1984)].

It is possible to generalize the effective potential method to include any system in which the electrons may be naturally divided into groups. Thus, the "valence" space becomes the group of electrons associated with some active part of the system, while the "core" becomes that part of the wavefunction that would normally be associated with "frozen fragments" in an all-electron calculation. The "frozen fragments" are represented by effective fragment potentials (EFP) much in the way frozen atomic cores are replaced by ECP.

While conceptually the same, the functional forms of EFP and ECP are quite different. The ECP are derived from atomic calculations, and the atomic symmetry allows the generation of the potentials to be reduced to a one dimensional problem. For the EFP, however, the frozen electron density is spatially distributed, and a one-center EFP expansion would naturally require many terms to achieve convergence. This difficulty is overcome by using a spatially distributed EFP expansion. We have developed an EFP method based on localized molecular orbitals (LMO). The coulombic terms are represented by distributed multipolar expansions at the LMO centers of charge, while the exchange terms are generated by direct optimization of parameters using a method similar to that used to in the generation of compact effective potentials for atoms.

The EFP method is designed to reproduce frozen fragment SCF calculations. However, it is possible to go beyond this limit by evaluating, perturbatively, the polarization of the "frozen" part of the system by the electric field of the "active" part. This has been accomplished by using distributed LMO dipole polarizabilities, also located at the LMO centers of charge. Examples will be presented for hydrogen-bonded systems in which one fragment is replaced by EFP and distributed polarizabilities.

+ 17

INVESTIGATION OF THE POLARIZATION OF MOLECULES IN AN INHOMOGENEOUS ELECTRON GAS MODEL

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The polarization of the electronic charge density in a molecule, under the influence of an external electromagnetic perturbation, is treated as a manifestation of non-zero momentum or current density. The variation in time of the external potential (due to motion of the nuclei or reaction with another species) causes a fluctuation in the electronic charge density. If this charge density is treated as a classical inhomogeneous electron gas, then certain external boundary conditions have to be imposed on this gas in order to correctly describe non-radiative processes.

24B

Connection between Supermolecular Møller-Plesset Treatment of the Interaction Energy in Weakly Bound Dimers and the Perturbation Theory of Intermolecular Forces

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This work presents a rigorous analysis of the MP2 and MP3 supermolecular treatments in terms of the perturbation theory of intermolecular forces. In order to connect the two formalisms the MP energies are first expanded in terms of an auxiliary double-perturbation theory similar to the one proposed by Sadlej (Mol. Phys. 33 1249 (1980)). In the next step, each term in this expansion is related to the perturbation theory of intermolecular forces in the formulation of Szalewicz and Jeziorski (Mol. Phys., 38 191 (1979)). The supermolecular MP2 interaction energy contains the second-order intrasystem correlation correction to the Coulomb energy, in addition to the UCHF dispersion. The supermolecular MP3 term involves the following: first-order intrasystem (apparent) correlation correction to the second-order UCHF dispersion, and third-order intramolecular correlation correction to the Coulomb energy. All terms are accompanied by their exchange counterparts. Numerical illustration of this decomposition is provided by calculations of interaction energies in He_2, $(HF)_2$, etc. The correction of supermolecular values by the full counterpoise procedure is shown to be essential.

24C

General contraction of Gaussian basis sets using atomic natural orbitals

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Abstract

The use of natural orbitals from atomic CI calculations to define generally contracted basis functions for correlated molecular calculations provides a means of exploiting very large sets of primitive Gaussians (including polarization functions) without the size of the contracted basis becoming unmanageable. Typically, ($13s\ 8p\ 6d\ 4f\ 2g$) primitive sets are used for first-row atoms, contracted to [$5s\ 4p\ 3d\ 2f\ 1g$]. Recent calculations using such sets will be reviewed, with particular emphasis on the calculation of molecular properties, and the extension of this approach to transition metals.

2 + D

Ab initio prediction of the vibrational spectra of unknown phosphorus compounds.

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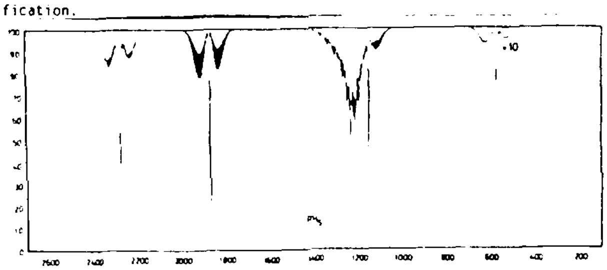
Ab initio SCF calculations at the 6-31G** level are reported for the fluorophosphines PH_nF_{3-n} (n=0-3) and the fluorophosphoranes PH_nF_{5-n} (n=0-5). The calculated geometries, vibrational frequencies, centrifugal distortion constants, Coriolis constants, and infrared band intensities are compared with the available experimental data, and good agreement is found in the case of the stable molecules PH_3, PHF_2, PF_3, and PF_5, particularly when the calculated force fields are scaled. The original assignments of the observed vibrational spectra are revised or extended for the molecules PHF_4, PH_2F_3, and PH_3F_2. Improvements to the current empirical force fields for PHF_2, PF_3, and PF_5 are suggested. The vibrational spectra of the unknown molecules PH_2F, PH_5, and PH_4F are predicted. Similar results are reported for the phosphine oxides R_3PO and phosphine sulphides R_3PS (R=H,F,CH_3). Plots of the calculated gas-phase infrared spectra at 300K with rotational fine structure are presented for the unknown molecules, as an aid to the experimentalists in the selective search for these molecules and their spectroscopic identification.



Calculation of NMR Shielding Constants for Fluorides and Oxides of Second and Third Row Elements by Coupled Hartree-Fock Perturbation Theory

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Ab initio Coupled Hartree-Fock Perturbation Theory (CHFPT) with large polarized Gaussian bases is used to calculate the NMR shielding constant tensors for a large number of fluorides and oxides of 2nd and 3rd row elements, such as B, C, Si, P and S. The computational method and a number of applications have been previously described (Tossell and Lazzeretti, J. Chem. Phys. 84, 369 (1986)). In this presentation the following categories of materials and general questions will be addressed:

(1) Systematics of shielding constant variations for well characterized materials.
  (a) Effect of number and identity of 1st coordination shell atoms upon the shielding, e.g., comparison of ^{31}P shieldings for PF_3, PF_4^+, PF_5, PF_6^-, PO_3^-, PO_4^{-3} and PF_3O.
  (b) Effect of changes in the 2nd coordination shell upon the shielding, e.g., ^{29}Si shielding in SiH_3OH, SiH_3OSiH_3 and $SiH_3OAlH_3^-$.
  (c) Effect of distortion from idealized geometries, e.g., ^{29}Si shielding of SiH_aF_b, a+b=4 and ^{31}P shielding of distorted PO_4^{-3}.
(2) Exploration of shielding trends for little studied nuclides, e.g., ^{33}S shieldings in sulfur oxides and polysulfur ions.
(3) Shieldings of transient and hypothesized species.
  (a) ^{29}Si shielding in H_2SiO and other multiply bonded Si species.
  (b) ^{29}Si shielding of species formed by incorporation of H and F into amorphous Si, e.g., $SiH_3FSiH_3^+$.
  (c) ^{11}B shielding of species occuring in borate glasses, e.g., BO_3^{-3} vs. $B_3O_6^{-3}$ (boroxol).
(4) Relationships of NMR shieldings to other spectral properties.
  (a) Paramagnetic shieldings and XANES in the SiH_aF_b series.
  (b) Changes in XANES and NMR shieldings due to Al for Si substitutions.
  (c) ^{17}O NMR shieldings, static dipole polarizabities and XANES of the BO_3^{-3} to NO_3^- series.

We will establish that we can explain well known shielding trends, calculate the shieldings of poorly characterized species with chemically useful accuracy and relate shielding trends to trends in other spectral properties.

24E

An Alternative Nonlocal Exchange Functional and its Influence on Calculated Bond Energies, Bond Distances and Spectroscopic Properties of Molecular Systems.

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Becke [Becke, A.; J. Chem. Phys. 1986, 84, 4524] has shown that the addition of nonlocal terms to the LSD exchange functional greatly improves the calculated value of bond energies of diatomic molecules. We have previously used Becke's exchange functional in the calculation of metal-metal bond energies in transition metal dimers and binuclear complexes [Ziegler, T.; Tschinke, V.; Becke, A.; Polyhedron, in press] as well as the M-H and M-CH_3 bond energies in transition metal complexes [Ziegler, T.; Tschinke, V.; Becke, A.; J. Am. Chem. Soc., in press], achieving reasonable agreement with experiment.

It has however become apparent that Becke's functional tends to over-estimate the value of bond distances and to under-estimate the value of bond frequencies. In an attempt to correct in part for the latter shortcoming, we propose an alternative nonlocal exchange functional which presents the advantage over Becke's of enforcing the value of the exchange density of any system to be always positive or null, in accord to physical requirements.

We assess the validity of our exchange functional by presenting some results for bond energies, bond distances and spectroscopic properties of various molecular systems.

4F

Ab Initio Study on the Bond Energies of Au(I) Complexes

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Ab initio SCF MO method has been applied to the calculations of the bond energies between Au^+ and various ligands such as Cl^-, I^-, and CN^-. The stabilization energies by hydration of Au^+, the ligands, and their complexes have been also calculated considering only their first hydration shell. The calculated bond energies indicate that, without hydration, Au-Cl bond is more stable than Au-I bond. Based on the concept of hard and soft acids and bases, however, in aqueous solution a soft metal ion Au^+ makes a more stable complex with a soft base I^- than with a hard base Cl^-. This discrepancy between the calculation and the experience suggests the importance of hydration effect, that is, stabilization by hydration of the ions and their adducts. The preliminary calculations considering hydration of AuCl and AuI show that their stabilization energies are determined mainly by hydration of Au atom with contribution from hydration of the halogen atoms being small. The comparison of the bond energies of various Au(I) complexes and the hydration effect on those bond energies will be discussed.

2 4 G

ACCURATE AB INITIO CALCULATIONS ON VAN DER WAALS MOLECULES -- THE HE DIMER --

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The He dimer is examined as a prototype system to establish the potential of supermolecular methods for the accurate calculation of potential energy surfaces for van der Waals systems.

- The (gaussian) orbital basis contains diffuse polarisation functions optimized for the dispersion energy in London's second order perturbation theory [1].
- The convergence of the first order (correlated) exchange repulsion with increasing basis is monitored using Symmetry Adapted Perturbation theory [2].
- The Basis Set Superposition Error (BSSE) is avoided using the Boys-Bernardi Counterpoise method [3]. The correctness of this approach is established by comparison with results from the BSSE-free perturbation theories [2,4].
- Multi Reference CI calculations are used to provide a correct evaluation of the dispersion energy [5]. Size consistency corrections are applied using an extension of Pople's method [6].

The final basis set contains the σ, π and δ components of up to h-functions as well as various sets of bond functions. This basis set yields a polarisation-dispersion energy of -17.02 K at 5.6 bohr, probably < 0.05 K above the limit and approaches the limit of the exchange repulsion from above to within 0.02 K. A 27 configuration reference set is sufficient to reproduce the full-CI interaction energy within the size-consistency corrected MR-CI up to $\pm$ 0.02 K. At 5.6 bohr, we obtain an interaction energy of -10.86 K, to be compared to a recent experimental result [7] of -10.94 K.

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* 1 Hartree = 315777. K

24H

Computed Potential Energy Surfaces for Chemical Reactions Relevant to High Temperature Air Chemistry and H_2 Combustion

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Recently a program has been started at Ames Research Center to compute, from first principles, rates for chemical reactions which are important in high temperature air chemistry and H_2 combustion. The high temperature air reactions are important in the shock layers which occur in front of hypersonic vehicles, while the H_2 combustion reactions are important in SCRAM jet engines, such as are being designed for the national aerospace plane (NASP).

Potential surfaces will be presented for selected reactions including:

$$N + O_2 \rightarrow NO + O$$

$$O + N_2 \rightarrow NO + N$$

$$H + O_2 \rightarrow HO_2 \rightarrow HO + O$$

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25H

HF-SCF, MC-SCF, and CI Calculations Using Selected Effective Core Potentials on Cu(II) Complexes: Copper Tetrachloride, Copper Oxide, and Copper Sulfide.

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A series of ten (Cu, Cl, and S) and eighteen (Cu) electron effective core potentials are employed in HF-SCF, MC-SCF, and CI calculations on the small model Cu(II) complexes: copper tetrachloride (D2h and D2d), copper oxide, and copper sulfide. The equilibrium geometries, low-lying excited state transition energies, and natural orbital populations are compared with results from all-electron calculations and available experimental data.

Ab-Initio Parameterization of Molecular Force Fields for Adrenergically Interesting Molecules

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ABSTRACT

WB-4101, 2-(2,6-dimethoxyphenoxyethylaminomethyl)-1,4-benzodioxane and various derivatives have been used extensively in the characterization of the alpha-1 adrenergic receptor. The large size of these molecules encumbers their rigid theoretical treatment. Molecular mechanic techniques provide a realistic alternative for preliminary conformational studies providing that an adequate parameterization is developed. Minimum basis set (STO-2G) geometry optimization followed by force field analysis was used to develop force constant information for aminomethyl-1,4-benzodioxane and 2,6-dimethoxy benzene, which are common structural components of the WB series. Force constant information obtained in this manner was used with the BIOSIM molecular simulation package to rapidly search the conformational energy surface of selected members of this series. Minimum energy conformers are verified with STO-2G energy calculations which were also used to provide MEP (Molecular Electrostatic Potential) maps and electronic densities. Comparisons of this technique are made to experimental X-ray crystal data and data obtained from semi-empirical (MNDO) calculations.

25C

EFFICIENT AB INITIO CALCULATION OF NMR CHEMICAL SHIFTS

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The most commonly used method of calculating NMR chemical shifts uses gauge invariant atomic orbitals (GIAOs), which are field-dependent basis functions, within the framework of Hartree-Fock perturbation theory. Current programs that use GIAOs are Ditchfield's, and Geissner-Prettre's, but they were written before the development of current techniques for the analytic calculation of the gradient of potential energy surfaces. These new developments can be used in an efficient analytic GIAO method.

There are several points at which the efficiency of chemical shift calculations can be improved:

(1) Elimination of the storage of the perturbed two electron integrals by calculating their contribution to a first order Fock matrix. Storage of these integrals requires a large amount of disk space and I/O time.

(2) Acceleration of the solution of the CPHF equations by a conjugate gradient technique, similar to the one introduced for this purpose by the Pople group for analytic second derivatives. These methods reduce the number of iterations needed for convergence by a factor of 2 or more.

(3) Calculation of the perturbed two electron integrals by an efficient technique, such as the McMurchie-Davidson algorithm or the Rys quadrature method of Dupuis and King.

(4) Omission of small contributions to the chemical shift, since the chemical shift doesn't need to be known beyond the accuracy of NMR instruments. The contribution of a shell of integrals can be efficiently estimated by the uncoupled Hartree-Fock theory using an effective density matrix approach. For large molecules, this is expected to be the most important saving.

Preliminary results and timings will be presented, as well as comparison with other methods, in particular the localized methods of Kutzelnigg *et al.* and Boumann *et al.*

25F

The Multiconfigurational Spin-Tensor Electron Propagator Method for Determining Vertical Principal and Shake-up Ionization Potentials for Open Shell and Highly Correlated Atoms and Molecules

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Abstract

We propose and develop the multiconfigurational spin-tensor electron propagator (MCSTEP) technique for the theoretical determination of vertical ionization potentials (IPs) and electron affinities (EAs) for general open-shell and highly correlated atoms and molecules. We obtain these equations from a Green's function or electron propagator approach where we properly couple electron removal and addition tensor operators to a multiconfigurational tensor state. To account for additional correlation and shake-up effects we include ionization and electron affinity operators analogous to the $|c\rangle\langle 0|$ state transfer operators necessary in multiconfigurational linear response. We further augment the initial MCSTEP operator manifold with operators of the form $a_i^+ a_j a_k$ by first employing perturbation theory and then repartitioning important operators into the primary space. In this way, important shake-up processes to diffuse orbitals are accurately and reliably handled at the same level of approximation, i.e. as part of the operator manifold. This method is known as the re-partitioned MCSTEP (RMCSTEP). Initial application of these methods is extremely encouraging for both principal and shake-up IPs. Using a <5s5p1d> contracted Gaussian valence basis set augmented with 2 diffuse s, 2 diffuse p and 2 diffuse d functions the ionization potentials to the low-lying (<~24 eV) ^2S and ^2P bound ionic states (including diffuse states) are calculated within ±0.07 eV of experiment for Be. The IP to the lowest ^2D state is calculated 0.14 eV from experiment.

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256

AB-INITIO STUDY OF THE LOW-LYING STATES OF FORMYLMETHYLENE(CHCHO)

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The lowest singlet surface of formylmethylene and other C_2H_2O isomers, ketene, oxirene, and hydroxyacetylene have been thoroughly studied[1] as part of an investigation of the Wolff rearrangement. However, little is known about the excited states of formylmethylene. In this study, features of the potential energy surfaces of the several low-lying electronic states at non-planar carbene, planar carbene and planar diradical structures of formylmehtylene have been investigated using MCSCF and multi-reference CI methods. In addition, the potential energy surfaces of three low-lying singlet states linking these structures were also examined in order to assess the stability of the possible local minima. It was found that the first excited state potential surface contain a local minimum which may have a reasonable life-time. This excited species has a planar diradical structure and is in the $^1A''$ state, lying 17 kcal/mol above the lowest sinlet state at the non-planar carbene strucuture. Unlike the lowest singlet species which is unstable with respect to the intramolecular rearrangement to ketene (the Wolff rearrangement), this excited species is stable due to the presence of the high potential energy barrier on the excited state pathway. Other salient features of the potential surfaces obtained will be presented and discussed.

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25D

Analytic Energy Third Derivatives for the Paired Excited Type of Multi-Configuration Self-Consistent-Field Wavefunction

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A theoretical formalism and its implementation are presented for the analytic evaluation of energy third derivatives for both closed and open-shell wavefunctions of the following three types: (1) two configuration (TC) self-consistent-field (SCF),[1] (2) generalized valence bond (GVB),[2] and (3) paired excited multi-configuration (PEMC) SCF[3] wavefunctions.

Analytic third derivative expressions for the general MCSCF wavefunction have been reported by several authors.[4-10] While these formalisms would be applicable to any type of MCSCF wavefunction, we have reformulated the third derivative expression for the above PEMCSCF wavefunctions using those conditions which are unique to these types in order to develop a more efficient implementation. The PEMCSCF wavefunctions are more easily constructed, because the computationally intensive four index transformation can be avoided in each SCF iteration. Additionally, subsequent procedures such as the computation of the AO part of the first, second, and third derivatives of the energy and the solution of the coupled perturbed (CP) PEMCSCF equations can also be carried out without having to do any four index transformations.

Relative to one configuration SCF wavefunctions, the PEMCSCF wavefunctions are found to result in significantly improved geometries, dipole moments, harmonic vibrational frequencies, infrared intensities, cubic force constants, and vibration-rotation interaction constants. The results for several small molecules with various basis sets will be presented and compared both with those using SCF wavefunctions and with experiment.

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25E

The Rôle of Distonic Radical Cations in Gas-Phase Ion Chemistry

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Gas-phase distonic radical cations have received considerable attention in recent years. The mass-spectrometric experiments of Professors McLafferty, Hammerum, Holmes and Schwarz have established the importance of these species in gas-phase processes. The results from our theoretical studies of a large number of distonic radical cations show that they are considerably more stable than their neutral counterparts and in some cases may even lie lower in energy than the isomeric conventional radical cations.

The fact that the distonic radical cations exhibit greater stability than their neutral counterparts has led to the realization that they can play a significant rôle in the reactions of gas-phase ions. We have used ab initio molecular orbital theory to investigate a number of such reaction systems. In this paper the results from a study of 1,*n*-hydrogen migration in simple ionized amines, including the radical cations of methylamine, ethylamine, *n*-propylamine and *n*-butylamine, are presented. The barrier heights for hydrogen migration decrease monotonically on progressing from the 1,2- to the 1,5-hydrogen shift. This smooth trend may be correlated in part with a decrease in ring strain and an increase in linearity of the calculated C---H---N angle in the corresponding transition structures. The calculated barriers and rate constants for hydrogen migration are consistent with facile rearrangements to distonic radical cations taking place in the gas phase in long-chain amine radical cations.

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Poster abstracts

Phase transitions and interfaces

(alphabetical by name of presenter,
which is underlined)

Brownian Dynamics Simulations of the Thermal Quenching of Argon Clusters.

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To determine the distribution of cluster geometries and energies as a function of quench rates, the results of Brownian dynamics simulations on Lennard-Jones representations of argon clusters will be presented. The simulations were performed by cooling the clusters from 120K to 0K for a variety of quench rates. For all quench rates studied, the lowest energy configuration had the largest population. The distribution of other clusters was not monotonic in energy, and some cluster configurations were nearly dynamically inaccessible. The correlation of the energy distribution with the structure of the cluster isomers will be shown.

A Study of the Pair Correlation Functions in the Liquid-Vapor Interface of Cesium and Sodium-Cesium Alloys by Monte Carlo Simulations

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ABSTRACT

Using the results of Monte-Carlo simulations of cesium, we demonstrate that the simple point local density approximation is inaccurate in predicting the transverse pair correlation function in the liquid-vapor interface of a simple metal. Our calculations demonstrate that a generalized local density approximation, such as the one proposed by Fischer and Methfessel, which uses the point density averaged over a region the size of the ions, more accurately describes the behavior of the transverse pair correlation function. We also find that in the liquid-vapor interface of several sodium-cesium alloys, the transverse pair correlation is independent of the bulk composition, even though the transition region from this sharp monolayer of pure cesium to the region of bulk composition is narrower than one atomic diameter.

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26C

On the Theory of Surface Bipolar Electrification
A New Consequence of the First and Second Thermodynamic Laws

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It is shown here that generally a surface, or a junction between any two media, has an electrostatically-charged dipole layer, which contains equal amounts of positive and negative charges. The media in question may be electrically conducting or insulating. At equilibrium, the potential difference across the surface cannot be measured directly with a voltmeter since the electric field, E, is conservative and gives rise to a vanishing emf around every mathematically-possible closed loop, including that of the voltmeter. Nonetheless, the existence of such undetectable surface charges may provide simple physical explanations for a number of common phenomena including: surface tension, adhesion, catalysis, surface wetting, and corrosion. Surface charges may additionally explain why, for example, generating static electricity is possible when some surfaces are rubbed against each other; and why aerosol and smoke particles are electrically charged; and why widening of microcracks in materials occurs with aging, causing possible degradation of mechanical, and electrical properties. In electrical insulators, these events could lead to lowering the breakdown voltage.

The surface electrostatic force, f_{es}, per particle is shown here to be $(5/3)\ \nabla\langle\varepsilon\rangle$; where $\langle\varepsilon\rangle$ is the average thermal kinetic energy per particle in the medium. Thus, inside a homogeneous medium, $f_e = 0$, and likewise $E = 0$. But at the surface, commonly $\nabla\langle\varepsilon\rangle \neq 0$, and therefore $f_{es} \neq 0$, and $E \neq 0$.

To arrive at such results, Sommerfeld's quantum-mechanical band is used. Particles of the media are considered to obey either the Fermi-Dirac or Bose-Einstein statistics. The procedure then involves what may be called the thermodynamic theory of generalized fields (TTGF).[1] In that formulation Maxwell's concept of a diffusion force[2] has been generalized, and its interaction with electric and other classical fields have been determined. In this paper, we shall show that this fundamental force has thermodynamic and quantum-mechanical origins, and then proceed to determine f_{es} on the basis of a novel application of Carnot's theorem. One application of TTGF, already worked out, involves conduction in semiconductor diodes.[1] Theory has accurately agreed with extensive experimental data reported by some 26 different authors over a period exceeding quarter of a century.

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26D

THE FREEZING AND MELTING BEHAVIOR OF NICKEL AND ALUMINUM IN THE EMBEDDED ATOM APPROXIMATION

by

S. M. Valone and J. E. Osburn

ABSTRACT

Over the last several years, a considerable effort has been expended using the "embedded atom" method (EAM) [1] for constructing an adiabatic potential energy surface for pure transition metals and their alloys. The method being semiemperical typically relies on low temperature information to fix the free parameters in the potential. While the method has been successful in describing, for instance, the grain boundary behavior of alloys [2] and the relaxation behavior of metal surfaces [3], it has yet to be concluded that these potential energy surfaces are adequate for describing higher temperature behavior such as the melting point of the transition metals and the alloys [4]. As an example, we will explore the melting behavior of pure Ni and pure Al as described in Refs. 2 and 3 and compare these to the behavior of the Lennard-Jonesian analogs [5].

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26E

FREEZING OF A DIATOMIC MOLECULE

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The freezing transition in a fluid of diatomic molecules is described by expressing the liquid-solid free energy difference as a functional of the inhomogeneous density of the solid. The theory predicts how the aspherical nature of the molecules affects the freezing density, as well as the translational and orientational distribution of the molecules in the solid. This talk presents theoretical results for a "hard dumbell" model for diatomics, a simple model that captures the effect of packing among aspherical molecules.

26F

Computer Simulations of the Free Energy of Physisorbed Films: Kr on Graphite

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The chemical potential of krypton monolayer and multilayer films on a graphite surface was calculated from computer simulations of the system using a suitably modified version of Widom's "particle insertion" technique. It is demonstrated that a local chemical potential exists in these strongly inhomogeneous fluids which is independent of position. It is also shown that a monolayer adsorption isotherm constructed from the simulations compares well with predictions based on the two-dimensional equation of state obtained from perturbation theory.

266

A Statistical Mechanical Model for Microemulsions

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Abstract

A microscopic statistical mechanical lattice model for microemulsions is presented whose energy parameters represent interactions among oil, water and surfactant molecules. Solving the model in the mean-field approximation allows phase diagrams and critical loci to be calculated. Features important in microemulsions are found in the model as well. These include ordinary critical, critical double point, critical endpoint, and tricritical loci, as well as three phase equilibrium. The homogeneity assumption is checked against the possibility of a stable lamellar phase.

Poster abstracts

The interface of electronic structure and dynamics

(alphabetical by name of presenter,
which is underlined)

26H

Theoretical Studies of Reaction Paths

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ABSTRACT

Calculations are described which involve a combined application of state-of-the-art electronic structure calculations and modern approaches to dynamics calculations to the abstraction reaction of H + CH_4. Focus is made on the most efficient and practical methodologies for these calculations.

27A

Group theoretical characterization of the pseudorotational quantum numbers of PF_5

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ABSTRACT

Fractional quantization of the adiabatic pseudorotation of isolated Na_3 has been observed experimentally and explained in terms of the geometrical phase predicted by M. Berry. The phenomenon of fractional quantization presumably occurs in other examples of pseudorotation having more complicated topologies. We seek to determine the nature of the rovibronic levels of one such case, PF_5, using group theoretical methods. Specifically, we consider the dimensions of the irreducible representations of O(3) x P, where O(3) is the group of rotations in three dimensions and P is the invariance group corresponding to the set of isomerizations of PF_5 that are achieved by pseudorotation.

ꓒ / E

A Semiempirical Method for Determining HyperRaman Scattering Intensities

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Recent advances in surface spectroscopy have enabled the straightforward measurement of hyperRaman spectra for a variety of adsorbates on certain metal surfaces. For many molecules, it is not possible to measure the corresponding bulk hyperRaman spectra, and because of this, the surface contribution to these spectra cannot be determined. One way to circumvent this problem is to evaluate the bulk intensities via molecular orbital methods, but since many of the molecules are quite large, standard _ab initio_ approaches are prohibitive. In this paper we present a semiempirical method for evaluating hyperRaman intensities, as well as related spectral information such as Raman intensities, polarizabilities and hyperpolarizabilities. The method has thus far been formulated using PPP wavefunctions, and in this case the evaluation of intermediate state sums is done directly, using singly excited configuration interaction calculations. Applications to pyridine will be discussed.

C

Deformation Resonance Approach to Adsorbate Induced Relaxation

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Adsorbate induced modifications of the surface lattice dynamics are of particular interest with respect to surface reconstruction and relaxation. We report on a theoretical attempt of disclosing the microscopic mechanism of an adsorbate driven change of the surface geometry in the early stages of adsorption. The theoretical framework is the deformation resonance approach, which has been developed for the investigation of inelastic gas - surface interactions. The adsorbate - phonon interaction is of short range and therefore treated in a localized basis set. The local deformation of the surface in the environment of the adsorbed particle is calculated self-consistently using quantum mechanics. Qualitative aspects of the correlated adsorbate - substrate motion are discussed paying special attention to the possibility of adsorbate induced soft phonon modes.

The method is applied to study the interaction of a hydrogen atom with the nickel 110 - surface. The three-dimensional static potential energy surface including the first and second derivatives with respect to substrate atom displacements has been evaluated using a sophisticated electronic model Hamiltonian. Many - body forces lead to a modification of the coupling between substrate atoms as compared to the clean surface. The metal atoms relax from their original equilibrium positions in order to minimize the total ground state energy of the interacting system. This behaviour is discussed as a possible driving force for the hydrogen induced reconstruction.

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DYNAMICAL CALCULATIONS ON THE PHOTOISOMERIZATION OF SMALL POLYENES IN A NONADIABATIC FORMALISM.

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On irradiation with (UV) light some unsaturated hydrocarbons may undergo cis-trans isomerization. In order to elucidate this process we examined the cis-trans isomerization of the (terminal) double bond of ethylene, butadiene and hexatriene.

Potential energy curves, (transition) dipole moments and nonadiabatic couplings (of the first 3-5 singlet states) for the twisting motion have been obtained from ab-initio/CI calculations. The nuclear wave functons have been calculated using an expansion method. The initially excited wave function is constructed from the eigenfunctions of the total Hamiltonian and the transition dipole moments of each vibrational level.

The states which carry oscillator strength show a minimum potential energy at a twist angle of 90 degrees. In addition butadiene and hexatriene have an energy barrier in the state (of resp. 1.9 and 4.1 kcal/mol). This causes the total number of vibrational levels contributing to the total wave function to decrease rapidly with increasing chain length, which accounts for the decreasing line width in the fine structure of the jet-cooled UV absorption spectra of these molecules (2).

The constitution of the total wave function determines the time development of the system as can be monitored by calculating the radiation- less decay: ethylene rotates very fast, butadiene somewhat slower and hexatriene is excited to an almost stationary state.

The calculations also show that in butadiene the A_g-state (the so called "hidden state") is rapidly populated as a result of a strong nonadiabatic coupling between the A_g- and the B_u-state.

Upon twisting of a double bond two Zwitterionic states with a large opposite dipole moment develop, but as a result of a nonadiabatic coupling these dipole moments cancel for all but the lowest vibrational levels of the lowest Zwitterionic state. As the total wave function consists only of higher vibrational levels and energy relaxation is not included in our present model, we do not find any substantial "sudden polarization".

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A General Polyatomic Potential Energy Surface Fitting Method

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A general technique will be presented which provides a systematic means for fitting polyatomic potential energy surfaces. Use is made of both *ab initio* energy and gradient data to fit the surface about an N-dimensional reference curve. The reference curve may be modified iteratively during the course of the fitting. A particular iteration will specify a new set of points which need to be calculated to improve the accuracy of the surface. The reference curve may be chosen to be the Intrinsic Reaction Coordinate of Fukui or some other curve which is deemed to be appropriate for the reaction.

The potential is fit in a Taylor series expansion of the form:

$$V(s,\mathbf{t}) = F(s) + \sum_{i} G_i(s)\Delta_i + (^1/_2) \sum_{i,j} H_{ij}(s)\Delta_i\Delta_j + \ldots.$$

where s is a suitably chosen reaction coordinate, **t** specifies the remaining coordinates, and $\Delta_i = t_i - T_i(s)$ is the distance away from the reference curve T(s). The function F and the elements of **G** and **H** are all represented by spline functions in s. F(s) is the energy along the reference path and is constrained to fit both the energy and derivatives exactly. Points not on the reference curve are least squares fit to determine the functions **G** and **H**. The current implementation of this method employs a global coordinate system and avoids uniqueness problems associated with describing the coordinates of a point.

Work supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under contract W-31-109-ENG-38.

27F

APPLICATION OF THE STABILIZATION METHOD TO THE TEMPORARY ANION STATES OF POLYATOMIC MOLECULES

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The stabilization method is used to estimate the energies and lifetimes of the temporary negative ion states of several polyatomic molecules including ethylene, formaldehyde, benzene, and various substituted benzenes. Electron affinities are determined using the Hartree-Fock and many-body perturbation theory procedures. Stabilization is accomplished by surrounding the molecule by a uniformly charged sphere of charge +q and radius R. The behavior of the eigenvalues of the anion/sphere system as a function of q and R is used to distinguish the resonance and continuum-like solutions.

This work was supported with a grant from the National Science Foundation

-276-

Determination of transition states and reaction path for chemical reactions

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A systematic search for transition structures can be performed carrying out walks along gradient extremals. Gradient extremals are lines connecting stationary points on the potential energy surface, and they are locally defined by the requirement that the molecular gradient is an eigenvector of the (mass scaled) molecular Hessian at each point on the line. At an equilibrium structure gradient extremals leave in all normal coordinate directions (positive and negative) and a systematical search for transition state structures requires a search along all these gradient extremals. In an appropriate mass scaled coordinate system gradient extremals may be used as the reaction paths in a simple description of the dynamics of a molecular reaction. We describe an algorithm to follow gradient extremals and we give some examples of the efficiency at which reaction paths and transition structures can be found with the algorithm.

27H

Abstract of a paper for the American Conference on Theoretical Chemistry, Gull Lake, MN, July 26-31, 1987

A New Potential Energy Surface for the $CH_3 + H_2 \rightarrow CH_4 + H$ Reaction

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We report a new semiempirical potential energy surface for the reaction $CH_3 + H_2 \rightarrow CH_4 + H$. The semiempirical calibration is based on *ab initio* electronic structure calculations and experimental thermochemical data, vibrational frequencies, reaction rate constants, Arrhenius parameters, and kinetic isotope effects. Variational transition state theory with semiclassical tunneling estimates is used in the design and subsequent testing of the new surface. We also provide a detailed factorization analysis of the kinetic isotope effects to illustrate the way in which various surface features contribute to the overall kinetic isotope effects. The new surface is consistent with most of the available experimental data. We report rate constants for the forward and reverse reaction, activation energies, and kinetic isotope effects for a series of temperatures calculated from the new surface.

This work was supported in part by the U.S. Department of Energy, Office of Basic Energy Sciences.

28A

AB-INITIO MRD-CI CALCULATIONS FOR THE PROPAGATION STEP OF CATIONIC POLYMERIZATION OF OXETANES BASED ON LOCALIZED ORBITALS

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We have carried out ab-initio MRD-CI (multireference double excitation - configuration interaction calculations by the technique of Buenker and Peyerimhoff into which we have also meshed a number of desirable computational options for ab-initio calculations on large molecules) for the initial cationic polymerization step of protonation of oxetane, for opening the oxetane and protonated oxetane rings and for attack of oxetane on protonated oxetane with concomitant opening of the protonated oxetane ring with both ab-initio all-electron calculations and ab-initio all-valence electron MRD-CI MODPOT calculations. The MRD-CI calculations for the protonation of oxetane demonstrated clearly that there are lower energy potential surfaces arising from the separated species oxetane$^+$ + H. In addition to studying oxetane plus protonated oxetane, we are studying energetically substituted oxetanes. The calculated potential energy surfaces indicate that a preferred pathway for this reaction resembles an S_N2 reaction with the oxygen of the oxetane attacking linearly along the C4-O direction of the protonated oxetane and inversion of the hydrogens around the C4 atom. We have been able to follow the reaction path and identify the transition state. The ring opening and reaction calculations were carried out with a new technique we had suggested and validated to include explicitly in the MRD-CI calculations the localized occupied and virtual molecular orbitals in the pertinent region and to fold the remainder of the occupied localized orbitals into an effective CI Hamiltonian.

This holds considerable promise for MRD-CI calculations for molecular decompositions and intermolecular reactions of large systems.

This research was supported by ONR, Power Programs Branch, Contract N00014-80-C-0003.

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2 8 B

To be presented at: 1987 American Theoretical Chemistry Conference, Cragun's Conference Center, Brainerd, Minnesota, 27-31 July 1987

New Insights into Chemical Reactions: The Reaction Path Model

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The concept of a *reaction path* which describes the continuous transformation of reactants into products is firmly embedded in the lore of chemistry. The reaction path has been rigorously defined (Fukui, *1970*) as the path of steepest descent in mass-weighted cartesian coordinates from the saddle point to reactants in one direction and to products in the other direction. Variations in the energy, geometry and vibrational frequencies along the reaction path, in addition to changes in the terms coupling motion along the path with the vibrational modes perpendicular to the path (the *coriolis* and *curvature* terms), form the basis of both variational transition state theory (Truhlar, Garrett & coworkers, *1980s*) and the reaction path Hamiltonian model (Miller, Handy & Adams, *1980*) of chemical reactions.

The reaction path model bridges the gap between electronic structure calculations of potential energy surfaces and the dynamics of chemical reactions. In addition to providing a quantitative basis for carrying out detailed dynamical studies, it provides unrivaled insights into the qualitative features of chemical reactions. We have computed reaction paths for a number of simple chemical reactions, determining all of the quantities necessary to carry out both variational transition state theory and reaction path Hamiltonian calculations. We will present the results of calculations on the following: Li + HF (a simple electron transfer reaction), $OH + H_2$ (a simple abstraction reaction), and $CH + H_2$ (a not-so-simple abstraction reaction).

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Work supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under contract W-31-109-ENG-38.

A Dynamical Model for Electron Transfer Reactions.

by

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We present a new approach for studying one of the most important chemical reactions, namely an electron transfer (ET) reaction. We present a model for describing the time-evolution of the ET-system, and also a variational scheme for selecting the initial state for the ET-system. In order to determine the ET-probability for a given donor and acceptor encounter-complex we use a non-linear TDHF-method based on an ab-initio electronic Hamiltonian.

We consider the ET-system to consist of an encounter-complex surrounded by the solvent; the encounter-complex consists of the donor, the acceptor and (optionally) a bridge/solvent compound. The surrounding solvent is described by a continous, linear, isotropic dielectric. The dielectric medium respons to changes in the molecular charge distribution inside the cavity. The bridge/solvent molecule inside the cavity represent the structural part of the solvent, where the outersphere of the solvent is treated as a dielectric medium.

When we include the bridge/solvent species in the detailed electronic structure study of the ET-system, we can describe in a proper manner bridge-assisted ET.

We consider the importance of donor-acceptor separation distance, encounter orientation, the outer dielectric medium, vibronic coupling and the structural part of the solvent.

THEORETICAL MODELS FOR AQUEOUS ELECTRON TRANSFER KINETICS*

28D

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The kinetics of electron transfer between metal ion complexes in aqueous solution is examined in terms of theoretical models which elucidate various aspects of activation and electronic coupling. These models are sufficiently flexible to permit detailed investigation of the roles of electronic structure, bimolecular encounter geometry, and solvent dynamics.

Calculations of electron transfer matrix elements based on many-electron ab initio wavefunctions for suitable molecular clusters provide the perspective for assessing the dependence of electronic transmission factors on donor/acceptor electronic structural properties, and the extent to which electron transfer reactions may be treated as effective "1-electron" processes. Depatures from a strictly 1-electron model arise from electronic relaxation when the donor and acceptor species are, respectively, oxidized and reduced, the main contributions being associated primarily with variations in the degree of ligand/metal covalency.

The degree of dominance of particular types of encounter geometry in bimolecular exchange kinetics has been examined, and new efforts have been directed toward providing a detailed account of short-range energetics when hexa-coordinate metal-ion complexes interpenetrate (in collaboration with H. L. Friedman et al. and N. R. Kestner et al.), following up earlier studies initiated by N. R. Kestner and P. Magestro.

An analysis of the behavior of dielectric continua (in collaboration with H. L. Friedman), is shown to yield straightforwardly an expression for solvent reorganization energy which clarifies its nature in terms of rigorous electrostatic quantities, and is also easily extended to accommodate solvent dynamics relevant to electron transfer. Specific application for the case of Debye dielectric dispersion yields helpful insight into the origin and role of the particular relaxation time which is relevant (i.e., the longitudinal time, τ_L).

Recent Publications

Comparison of Electron-Transfer Matrix Elements for Transition-Metal Complexes: t_{2g} vs e_g Transfer and NH_3 vs. H_2O Aquo Ligands, M. D. Newton, J. Phys. Chem. 90, 3734-3739 (1986)

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Current Views of Hydrogen Bonding from Theory and Experiment — Structure, Energetics, and Control of Chemical Behavior, M. D. Newton, Transactions of the ACA (1987)

* This research was carried out at Brookhaven National Laboratory under contract DE-AC02-76CH00016 with the U. S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

Quasi classical study of the dynamics of three atom-exchange indirect exoergic reactions.

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Indirect exchange reactions of the type A + BC --> AB + C have been much less investigated than direct ones from the dynamical point of view. The building of flexible models representing the potential energy surfaces (PES) which exhibit an intermediate well of variable anisotropy allows to determine, by quasi classical trajectory (QCT) method, the distribution of the energy of the reaction on the nuclear motion modes of the products i.e. mainly the vibration of AB and the translation of C with respect to AB. The rotation of AB represents a small part of the energy disposal, provided that the intermediate complex is linear. The conclusions of this study realized mainly at 1D level corresponding to almost equal masses (12,14,16 a.m.u.) are the following :

a) It exists a domain of low anisotropy of the well for which all the trajectories submitted are direct (double bounce motion in the well). The intermediate complexes have short lifetimes (roughly 2 or 3 times the vibrational period of BC). In this domain, the average vibrational energy deposed on AB is a continuous function of the anisotropy of the well which is connected to the location of the minimum of this well according to the empirical law proposed by Herschbach and Laurie. It turns out that the greater the anisotropy of the well, the larger the vibrational excitation of AB is.

b) This domain is surrounded by a region corresponding to a greater anisotropy characterized by a discontinuous relation between the average vibrational energy of AB and the anisotropy of the well.

As long as we move away from the regular domain, the trajectories are more and more snarled leading to longer and longer lifetime complexes and an increasing number of non reactive outcomes. Although the relation between the average vibrational energy of AB and the anisotropy of the well is non regular, it turns out that the reactive events are associated to higher vibrational excitation of AB, as long as the anisotropy increases.

The reaction $C(^3P)$ + $NO(X^2\Pi)$ --> $CN(X^2\Sigma^+)$ + $O(^3P)$ appears to be a good example of the regular behavior associated to a well of moderate anisotropy.

Abstract of a paper for the American
Conference on Theoretical Chemistry,
Gull Lake, MN, July 26--31, 1987

28F

Quantum Mechanical Calculations of Vibrational Energy Transfer Probabilities for Molecular Collisions

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Abstract

We have carried out quantum mechanical dynamics calculations for vibrating rotator collisions of two hydrogen fluoride molecules. These calculations are for a total angular momentum of zero and make no dynamical assumptions. The potential energy surface is a new analytic representation of extensive *ab initio* data (over 1400 points). The analytic representation has several important features among which are an accurate representation of vibrational forces and very efficient evaluation for the quantum calculations. The calculations were performed efficiently using the R-matrix propagation algorithm vectorized for the Control Data Corporation Cyber 205 vector pipeline computer. Several basis sets with 694-1358 channels are used to demonstrate the convergence of the calculations.

The calculations show that for the process

$$HF(v_1 = 1, j_1 = 0) + HF(v_2 = 1, j_2 = 0) \rightarrow HF(v_1' = 2, j_1') + HF(v_2' = 0, j_2')$$

a large amount of rotational excitation accompanies the vibrational quantum number change. A simple energy gap prescription does not account for the final state distributions. Detailed results will be presented as well as comparisons to results obtained on other potential energy surfaces.

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Geometrical Energy Derivative Evaluation with MRCI Wave Functions

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Abstract: A progress report will be presented on the implementation of an analytic geometrical energy gradient method designed to be efficient for large scale multireference configuration interaction wave functions (*Int. J. Quantum Chem.* **31**, 33 (1987)). The gradient computation requires the evaluation of the equation

$$E^x = Tr(\mathbf{h}(ao)^x\, \mathbb{D}(ao)) + {}^1/_2\, Tr(\mathbf{g}(ao)^x\, \mathbb{d}(ao)) - Tr(\mathbf{S}(ao)^x\, \mathbb{F}(ao))$$

for each coordinate direction "x". The two- and four-index arrays $\mathbb{D}$ and $\mathbb{d}$ are effective density matrices and the two-index array $\mathbb{F}$ is an effective Fock matrix, all represented in the AO orbital basis. This equation is identical to that required for the analytic gradient evaluation for simpler wave functions, such as single configuration and multiconfiguration SCF, except that for these cases the actual density matrices are used instead of the effective density matrices. The matrices $\mathbb{D}$ and $\mathbb{d}$ are defined as $\mathbb{D}=(\mathbf{D}^{ci} + \mathbf{D}^{\Lambda} + 2\mathbf{D}^{\lambda})$ and $\mathbb{d}=(\mathbf{d}^{ci} + \mathbf{d}^{\Lambda} + 2\mathbf{d}^{\lambda})$ and the matrix $\mathbb{F}$ is defined from $\mathbb{D}$ and $\mathbb{d}$ in the usual way. This method is particularly attractive for large scale MRCI wave functions because no component of the gradient evaluation is explicitly proportional to the number of coordinate directions. The bulk of the computational effort required with this method is for the construction of the components of the effective density matrices which are coordinate independent. The details of this construction and timing results where available will be discussed.

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[b] Supported by the Austrian-American Educational Commission (Fulbright Commission).

28H

Desorption by Electronically-Stimulated Adsorbate Rotation,*

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We have used time-of-flight laser resonance-ionization to measure state-selective translational energies of neutral NO and CO desorbed from Pt(111) following electron impact. We found evidence for a very low-energy desorption channel which dominates neutral NO production and whose peak translational energy is only .05eV. The threshold (near 6eV) of this low-energy channel correlates with a single-particle excitation. In contrast this channel is relatively absent for CO.

Here we present a theoretical model supported by lifetime (electronic-structure) and dynamics calculations which suggests a novel mechanism to explain these experimental observations. By computing the lifetimes for possible single-particle excitations we are able to eliminate all but the 5σ hole as substantially contributing to the observed yield since the 5σ hole is the only one-electron excitation which due to its symmetry is relatively long lived (>10(-14) sec). We argue that such an excitation in CO does not cause desorption, as the screening of the hole by the metal increases the number of 2π electrons. This makes excited CO electronically resemble ground state NO (in its bonding character) which bonds similarly (terminally and strongly bound 1-1.5 eV). By the same argument, excited NO would resemble O_2 and thus have a much weaker bond and consequently a relatively unhindered rotation (O_2 is bound side-on by only ~.3eV). If the hindered-rotor to free-rotor transition is not considered, excitation decay retraps the NO with high probability. However, the inclusion of the rotational degree of freedom allows excited NO to access weakly bound regions of the ground state potential energy hypersurface. Thus, desorption occurs in a two-step (analogous to resonance Raman) process: the initial, strongly bound, hindered-rotor ground state makes a transition to a long-lived, weakly bound and relatively free-rotor excited state, followed by a second transition to a continuum level of the ground state potential. An R-matrix calculation is developed and presented here which closely reproduces the observed translational and rotational energy distributions. This fact is particularly significant because the potential parameters were chosen to agree with independent experimental observables, other semi-empirical surfaces and ab-initio calculations and not adjusted to fit our stimulated desorption observations. This indicates that the 5σ hole does indeed cause the hindered rotation of ground state adsorbed NO to be freed.

Some interesting stability questions due to the bound state character of the final state arise in the R-matrix calculation. These will also be discussed.

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Abstract of a paper for the
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Determination of Rotationally Inelastic Cross Sections for He-I_2 Scattering by Quasiclassical Trajectory Methods

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Abstract. We are currently investigating rotationally inelastic cross sections for the scattering of I_2 by He as a function of initial relative translational energy. Comparison of earlier quantum mechanical predictions of He-I_2 vibrational excitation cross sections [1,2] with experimental results [3] suggest that the potential energy surfaces [2,4] used originally may exhibit incorrect anisotropy. We have improved the second (*ab initio*) surface, and we are performing quasiclassical trajectories on this potential surface to calculate state-to-state rotationally inelastic cross sections for this system. These cross sections will be compared to new experimental data [5] in order to further test and refine the anisotropy of the potential.

This work was supported in part by the National Science Foundation and the Minnesota Supercomputer Institute.

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α7B

(Presented at the American Conference on Theoretical Chemistry, held July 27-31 at Gull-Lake, Minnesota, USA)

A realistic $HO_2(X,{}^2A")$ potential energy surface from the double many-body expansion method

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Recently[1], we reported a potential energy surface for the electronic ground-state of HO_2 from the double many-body expansion (DMBE) method. This potential conforms with the ab initio data of Melius and Blint[2] for the three-body energy, and shows good agreement with available spectroscopic data for the energy and geometry of the minima referring to the equilibrium triatomic. It also shows the expected R^{-n} behaviour at the asymptotic channels being the electrostatic O-OH interaction energy defined in the spirit of an adiabatic theory recently proposed by Clary and Werner[3].

Despite the fact that the potential of Ref.1 shows some definite improvements over previous functions, it is not completely satisfactory. In particular, exploratory quasiclassical trajectory calculations[4] for the $O+OH\rightarrow O_2+H$ reaction have yielded thermal rate constants in poor agreement with experiment. Our aim in the present work is therefore to report an improved DMBE HO_2 potential which overcomes such deficiency. A perhaps more satisfactory adiabatic theory is also suggested to describe the O-OH long-range electrostatic interaction energy. In addition, we show how to make the potential reproduce the complete experimental quadratic force field of the hydroperoxyl radical and yet give quasiclassical thermal rate constants[4] in good agreement with the best reported measurements.

This work was supported by the Instituto Nacional de Investigação Científica (INIC), Portugal, and a Portuguese-Spanish joint venture (Acção Integrada). L.A.M.Q. thanks the Ministerio de Educacion y Ciencia, Spain, for a FPI grant.

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Bifurcations on Energy Surfaces Governing Chemical Reactions

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When a chemical reaction reduces the molecular symmetry, then one reactant, having C_s symmetry say, goes into two products which are transformed into each other by the C_s operation. Consequently a *bifurcation* occurs along the reaction path. Orthogonal trajectories of energy contours (steepest descent curves), which are often taken as schematic, nondynamic model patterns for reaction paths (IRC's), are of limited use for the elucidation of this phenomenon because, for many bifurcations, there exists *no* orthogonal trajectory pattern which could serve as a realistic model. This limitation aries from the fact that the orthogonal trajectories themselves can bifurcate *only* at reactant sites and at transition states where, in addition to all derivatives vanishing, the hessian has *two* zero eigenvalues which is a *very* rare occurrence. The critical points for bifurcations are those points on the reaction surface where a valley turns into a ridge, or where a cirque turns into a cliff. Higher order Taylor expansions around such points show that three distinctly different types of surface topographies exist when bifurcations and transition states lie close together. They correspond to the former occurring before, at or after the latter. If the bifurcation occurs at or after the transition state, then there exist no steepest descent lines descending from the transitionstate through a valley to the products. It is quite possible that bifurcations and transition states lie very close to each other, forming a *bifurcating transition region*. The general formal analysis is confirmed by an examination of the energy surface for the ring opening of cyclopropylidene to allene. In this instance the bifurcation lies so close to the transition state that it changes from "before" to "after" when the atomic orbital basis set is changed from a minimal (STO-3G) to an extended (3s2p1d) basis

Acknowledgment

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Theoretical Study on Mode-Selective Chemical Reactions in Cryogenic Matrices

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Classical trajectory calculations are performed for the isomerization reaction of the HCN molecule in the cryogenic Ar matrix. Our theoretical model consists of the twelve first shell and the 42 second shell Ar atoms which surround a central HCN molecule. The potential surface of isomerization is described by the Murrell-Sorbie function and the interactions between HCN and Ar and between the Ar atoms are represented by the Lennard-Jones potentials. We discuss the mode-selectivity of the process based on non-RRKM behaviors of lifetime distributions obtained by selective excitations of the CH and NH overtone modes.

Poster abstracts

Spectroscopy and optical properties

(alphabetical by name of presenter, which is underlined)

2?E

VIBRATIONAL CIRCULAR DICHROISM AND LOCAL MODE VERSUS NORMAL MODE BEHAVIOR

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Abstract

Vibrational circular dichroism (VCD) may at times provide a useful criterion for distinguishing between local mode and normal mode behavior. This assertion is based on the notion that the generation of significant VCD intensity among a set of dissymmetrically disposed, locally achiral oscillators (e.g., CH-oscillators) normally requires kinetic and potential energy couplings of the sort associated with normal mode behavior.

VCD measurements have been performed for the fundamental[1] and for the second and third overtone CH-stretching regions[2] in a set of terpenes and related compounds. The data suggest normal mode behavior in the overtones of some compounds, but not in others. Model calculations are presented which attempt to provide some understanding for the observed data.

We are grateful for support from the Programma Strategico Dinamica Molecolare e Catalise del C.N.R. and the National Science Foundation.

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D_2 Raman Line Shapes Broadened by He

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ABSTRACT

The calculation of the pressure dependence of the D_2 Q branch of Stokes Raman line shapes is presented and compared with some experimental results. These line shapes are determined from the Fourier transform of an off-diagonal element of the density operator,[1] which, in turn, is found as a solution of the Waldmann-Snider kinetic equation. The collision portion of this equation was determined from an ab initio D_2-He interparticle potential[2] averaged over D_2 vibrational wavefunctions. These latter wavefunctions were also calculated with an ab initio D-D potential.[3] Thus, there were no adjustable parameters for the line shape calculations. In the high pressure limit, the calculated line widths matched the experimental line widths[4] to about 5%.

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2916

Applications of the adiabatic approximation in vibrational spectroscopy

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The adiabatic approximation is applied to several problems in vibrational spectroscopy. An adiabatic method of incorporating harmonic bending and stretching modes into the local mode model is developed. Simple formulae for spectroscopic constants are obtained. The formuale are shown to reproduce well the experimental results for H_2O, H_2S and H_2Se and are tested against previous calculations. The adiabatic approach is also used to study Fermi resonances in CHX_3 molecules. The Hamiltonian is written in terms of symmetrized curvilinear internal coordinates and their conjugate momenta; the G matrix is expanded in the displacement coordinates and the terms most important for the Fermi resonance problem are retained. Nonadiabatic effects are explicitly considered.

AB INITIO COMPUTATION OF INFRARED AND VIBRATIONAL CIRCULAR DICHROISM ABSORPTION INTENSITIES

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Vibronic coupling theory can be used to estimate infrared and vibrational circular dichroism absorption intensities. Using ab initio, single determinantal wave functions we will present the implementation of the model by L.A. Nafie and T.B. Freedman (1) for the computation of the dipole strengh (ir intensity), and the rotational strength (vcd intensity) of small molecules. A number of calculations on simple systems will demonstrate and contrast different approaches, such as using the dipole momentum rather than the dipole length operator, or approximating electronic excitation energies by an average energy difference. We will also draw some comparisons between these results and less accurate computations using fixed partial charges on each atom (2).

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3 O H

Transient, collision-induced changes in molecular dipoles and polarizabilities

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During collisions between molecules in a gas or liquid, the charge distributions of the colliding partners distort, causing transient changes in the molecular dipole moments and polarizabilities. These changes are manifested in the occurrence of single-molecule forbidden IR and far-IR absorption, interaction-induced light scattering, collisional effects on lineshapes for allowed scattering or absorption, and density dependence of dielectric and optical properties. Thus calculations of collision-induced dipoles and polarizabilities as functions of intermolecular separation and relative orientation not only provide information on the charge redistribution due to nonbonding interactions, but also make it possible to extract further information on dynamics in condensed media via spectroscopic lineshape analyses.

Our recent work has focused on the effects of van der Waals interactions on molecular properties, and on the effects of the distribution of polarizable matter throughout the interacting species.

We have developed a reaction-field theory for the van der Waals contributions to molecular properties; and it suggests a new physical interpretation of these contributions. As in earlier models, each molecule is hyperpolarized by the combined effects of an external field and the field from the fluctuating charge distribution of its neighbors--but in addition, the external field modifies the correlations between the spontaneous, quantum mechanical fluctuations in the charge density of each molecule. We have derived accurate integral expressions for the van der Waals induced properties, and approximations in terms of static susceptibilities and van der Waals interaction energy coefficients. Numerical results have been obtained for atom-diatom and diatom-diatom pairs containing He, H_2, and N_2.

We have also developed a polarizability density model that reflects the distribution of charge within interacting molecules. In this model, we employ nonlocal response tensors (linear and nonlinear) to obtain the polarization induced at one point in a molecule, due to the application of an electric field at other points. Recently we have found a method of calculating the nonlinear response tensors that determine collision-induced dipoles: we require only the first-order correction to the molecular wave functions in a uniform external field, and auxiliary functions used to compute van der Waals interaction energies. By exploiting atomic symmetry, we have derived a compact new equation for the van der Waals dipole of a heterodiatom, with overlap damping included.

303

Vibrational Frequencies and Intensities of H-Bonded Systems. 1:1 and 1:2 Complexes of NH_3 and PH_3 with HF

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Frequencies and intensities are calculated by ab initio methods for all vibrational modes of the 1:1 H_3X-HF and 1:2 H_3X-HF-HF complexes (X=N,P). The HF stretching frequencies are subject to red shifts, roughly proportional to the strength of the H-bond, and to manyfold increases in intensity. Although the intramolecular frequency shifts within the proton acceptors are relatively modest, the intensities of the NH_3 stretches are magnified by several orders of magnitude as a result of H-bonding (in contrast to PH_3 which exhibits little sensitivity in this regard). The frequencies and intensities corresponding to bending of the H_3X-HF H-bond rise with increasing H-bond strength while the properties of the other intermolecular modes appear somewhat anomalous at first sight. The intensity patterns are analyzed by means of atomic polar tensors which reveal that intensification of the proton donor stretch is chiefly due to increasing charge flux associated with H-bond formation. The different behavior of the N-H and P-H stretching intensities is attributed to the opposite sign of the hydrogen atomic charges in the two molecules. As a general rule, low intensities can be expected for intermolecular modes with the exception of those which involve motions of hydrogens that appreciably alter the magnitude or direction of a subunit's dipole moment.

ELECTRON-CORRELATION EFFECTS ON ONE-PHOTON TRANSITION PROBABILITIES IN f^N SYSTEMS

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The intensity data of electric-dipole transitions in rare earth systems are traditionally analyzed by means of the Judd-Ofelt theory [1,2]. In this theory the f↔f transitions are considered to be forced and their occurrence is due to the mixing of higher energy configurations of opposite parity via the odd terms of the crystal field. The semiempirical realization of the Judd-Ofelt theory turned out to be a useful tool for identification of the majority of observed transitions. However, all attempts to reproduce the experimentally determined parameters by ab initio calculations have met with little success. Therefore most of the recent theoretical studies aspire to clarify which mechanism causes the greatest modification of the Judd-Ofelt parameters.

The details of the electronic structure of the rare-earth ion have been introduced into the f↔f transition theory through the third-order contributions to the transition amplitudes [3,4]. These new terms represent electron correlation inside the central ion and they originate from static and dynamic models assumed for all interactions between the ion and its surrounding ligands.

The various aspects of the influence of electron correlation upon the transition amplitudes have been analyzed in detail [5,6]. The discussion has been based on the numerical results of ab initio calculations performed within the perturbed-function approach [7] for Pr^{3+}. In general, it has been shown that the third-order contributions due to electron correlation cause a significant modification of the second-order transition amplitude. Thus, the importance of electron-correlations effects has been established beyond doubt and, therefore, one may conclude that in any reliable theory of the f↔f transitions these effects should be taken into account.

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30 D

The Electronic Transition at 5370 Å for the Copper Trimer

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Obtaining and assigning the electronic spectrum of Cu_3 is a subject of much recent interest. Two-photon ionization and other techniques[1] have provided a vibrational spectrum in an electronic state 2.30 eV above the $^2E'$ ground state. This has been tentatively assigned as a $^2E''$ state. Laser-induced fluorescence has yielded the vibrational structure of the ground state.[2]

An $E \otimes e$ Jahn-Teller model truncated to quadratic terms has been used by the present authors and others[3] to fit the vibronic spacing within both electronic states and hence to assign the spectra. The parameters of the model are adjusted to predict the lower levels of a given electronic state within experimental uncertainty and are then used to predict the higher levels. This method yielded excellent results for the upper electronic state (predicting 14 levels quite well although the parameters were fit to only four), thus adding credence to the $^2E''$ assignment. The ground state, having a larger Jahn-Teller stabilization energy and therefore more anharmonicity, was also well fit.

The present study looks at both of these electronic states simultaneously. Frank-Condon factors are used to study intensities for *both* emission and absorption to more fully understand the symmetries and quantum numbers of these vibronic states and to refine further the two potential energy surfaces.

This work was supported in part by the National Science Foundation.

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Surface Enhanced Resonance Raman Scattering of Cobalt Phthalocyanine Dye on Ag Island Films: Two Electromagnetic Theory Models

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ABSTRACT

We present a combined experimental/theoretical study of the coverage and frequency dependence of surface (enhanced) resonance Raman scattering (S(E)RRS) of cobalt phthalocyanine (CoPc) on silver island films. The experimental work indicates a rather strong coverage dependence at very low coverage, with a peak at 0.07 ML followed by a rapid decrease above that. At very low coverage S(E)RRS enhancements comparable to SERS are observed. To model this coverage dependence, we consider the electromagnetic interactions between the adsorbate and substrate, with the substrate modelled as a metal spheroid and the adsorbate as a layer with variable coverage. Two models for this layer are considered, an effective medium model and a coupled dipole model in which both the molecules and metal are then to be dipoles. The dependence of field enhancement and S(E)RRS intensity is studied for these two models as a function of frequency, coverage, stokes shift, adsorbate size, and spheroid size. It is found that although there are differences between the two models, the coverage dependence is similar at the peak intensities at about 0.1 ML for reasonably prolate spheroids. This indicates that the drop in intensity above 0.1 ML arises from damping of the plasmon resonance by the adsorbed layer. Interadsorbate interactions are found to play a role in determining the coverage dependence of the S(E)RRS intensity that is secondary to this damping. The large enhancements seen below 0.1 ML adsorbed CoPc suggest that excited state quenching by the surface is not important in this nonfluorescent molecule.

Poster abstracts

Other topics in theoretical chemistry

Association reactions
Clusters
Computer programs
Density functional theory
Fusion
Kinetics
Molecular Biochemistry
Particle interactions
Periodic table
Polymers
Vibrational relaxation

(alphabetical by name of presenter, which is underlined)

3F

THEORETICAL MODEL CALCULATION OF THE VIBRATIONAL RELAXATION OF A DIATOMIC MOLECULE ADSORBED ON A SURFACE

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The vibrational relaxation of a diatomic molecule adsorbed on a surface is studied using a quantum mechanical model which represents a significant improvement over a simple multiphonon mechanism. The intramolecular vibrational motion has a frequency which is assumed to be much higher than the phonon frequency and it is described as a two -level system. The molecule-surface adbond is taken to be a temperature-dependent, renormalized Morse oscillator which is anharmonically coupled to the fluctuating bath. The bath is a Debye distribution of harmonic oscillators with a finite lifetime (to phenomenologically account for phonon-phonon and possible phonon-electron interactions). Projection operator techniques are used to derive an equation of motion for the population of the upper vibrational state. This is then solved to second-order in the bath-molecule interaction. However, the usual Markovian approximation is not made, so that a direct numerical check can be done on its validity. We find that this approximation is very good for the particular system studied (OH on SiO_2). A quantitative measure for the breakdown of the Markovian assumption is also given.

The relaxation rate can be written as a sum of contributions from different channels. These channels consist of: I) near resonance energy transfer from the molecular vibrational mode to the adbond, accompanied by low-order (one or two phonons) emission/absorption of phonons such that the total energy is conserved; II) off-resonance transitions with high-order multiphonon processes (up to four phonons were considered). The results of the calculation are in good quantitative agreement with the experimental results of Casassa et al. (J. Chem. Phys. 84, 2361). In particular, the model can partially account for the anomalous isotope effect which was reported. However, for a full understanding of this effect, the coupling to the other vibrational modes of the molecule-surface system must be taken into account.

3 1 6

A graphical tool for chemists

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Abstract

Theoretical chemists have been taking advantage of computer generated graphical displays ever since they became available. After all, drawings are usually much easier to interpret than raw data. Practically every chemist is now familiar with contour plots or surface projections. They both represent 2D data, f(X,Y), even though the surface is drawn in 3D perspective. Recent developments in computer and graphics hardware and software make it fairly easy to display true 3D data, f(X,Y,Z). As a matter of fact, there are several such specialized systems currently used, for example Hehre's electron density analysis package or a variety of programs used in molecular modelling. Unfortunately, these sophisticated tools require either expensive hardware or software, or both.

3-dimensional objects can be represented by solid surface displays or by less spectacular but easier-to-draw chicken-wire plots. A widely used example of the latter is Jorgensen's PSI77 program. In our lab, we have developed a new program to produce chicken-wire plots using one of the newer ACM algorithms. This easy-to-use and versatile package will soon be available to the general public. Our program can be executed either interactively or in batch and is used to produce plots of molecular orbital wavefunctions, single MO densities, partial or total molecular densities, electron density differences, Van der Waals surfaces, and any other function of three variables. This program can be easily interfaced with GAUSSIAN 80 or 82, MONSTERGAUSS, POLYATOM or any other program.

In the current implementation, our program uses the intelligence of TEMPLATE device drivers to run on a wide range of graphics terminals, plotters, and workstations. It can also be executed in the native mode of plotters like CALCOMP using their vendor software.

Since the major problem of displaying this type of function is that only one isosurface can be viewed at a time, our program has built-in capabilities to store several isosurfaces as segments and then display them in a sequence (animate if the hardware allows for that).

The presentation will demonstrate typical applications of this package.

304

Electrostatic Models of Enzyme-Ligand Association

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The rate of catalysis of many enzyme-substrate systems appears anomalously large when one considers that the reactive site is buried in the bulk of the protein, and is small relative to the size of the protein. The low activation energy of these enzymatic reactions suggests that the reaction mechanism is diffusion-controlled, and that protein-substrate recognition may actually begin in the initial stages of diffusion where electrostatic interactions dominate.

We present a study of the effects of electrostatics on the rate of ligand-enzyme association by investigating analytical electrostatic models having a continuous dielectric or a dielectric discontinuity between the protein-solvent interface. The rates of diffusional association were calculated using Brownian dynamics on the system representing Superoxide Dismutase (SOD)/Superoxide, although the general form of these models will be applicable to other systems.

SOD is an overall negatively charged enzyme (-4e) which oxidizes the superoxide radical to hydrogen peroxide and oxygen at rates close to diffusion-controlled. We have found that the electrostatic models which distinguish the protein interior from that of the surrounding solvent enhance the rate of binding 60% over the continuous dielectric cases. This enhancement is attributed to a "lensing effect" brought about by the change in dielectric constant at the curved boundary defining the protein-solvent interface. The resulting lines of repulsive force are focused in such a manner as to steer the superoxide ligand into the active site of SOD in a much more dramatic fashion than that of the continuous dielectric models.

Ionic strength dependence on the rate of binding was also examined through the introduction of extended Debye-Huckel (DH) theory. Experiments have shown that the rate of catalysis of SOD/Superoxide diminishes with increasing ionic strength. Both the continuous dielectric (CD-DH) and dielectric discontinuity (DD-DH) models were able to realize this trend. Only the DD-DH case was able to predict the correct asymptotic behavior at infinite ionic strength in which all electrostatic forces are screened and the rate is diffusion-controlled. An inherent flaw of the continuous dielectric models is that at zero ionic strength the rate of binding is less than diffusion-controlled.

We have reached the conclusion that models with a dielectric discontinuity provide a more reliable means of elucidating the primary mechanisms of electrostatic interactions in diffusion-controlled reactions involving protein systems. We plan to extend our investigations to other proteins such as Ribonuclease A.

31A

REACTION FREE ENERGY PROFILES IN SOLUTION. S.E. Huston, P.J. Rossky
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Comparison of the free energy surface of a chemical reaction in solution with that in the gas phase can be useful in illustrating the specific effects of a solvent medium on a reaction. Solvation of the reactant species may produce qualitative as well as quantitative changes in the nature of the surface.

The extended RISM integral equation allows calculation of the relevant thermodynamic quantities from knowledge of the site - site interaction potentials for polar solutions. In addition to providing qualitatively reliable results at a small fraction of the cost of computer simulation methods, the theory allows calculation of full energetic and entropic reaction profiles, information that is difficult to obtain from simulation.

Extended RISM studies of the reversible work surfaces for the S_N2 reaction of m thyl chloride with chloride and the S_N1 reaction of tert-butyl chloride, both in aqueous solution, will be presented. Results include investigations of the influence of solvent polarity and reactant charge transfer rates.

AD-A195 520 AMERICAN CONFERENCE ON THEORETICAL CHEMISTRY HELD IN GULL LAKE MINNESOTA ON JULY 25-31 1987(U) MINNESOTA UNIV MINNEAPOLIS D G TRUHLER 1988 AFOSR-TR-88-0420

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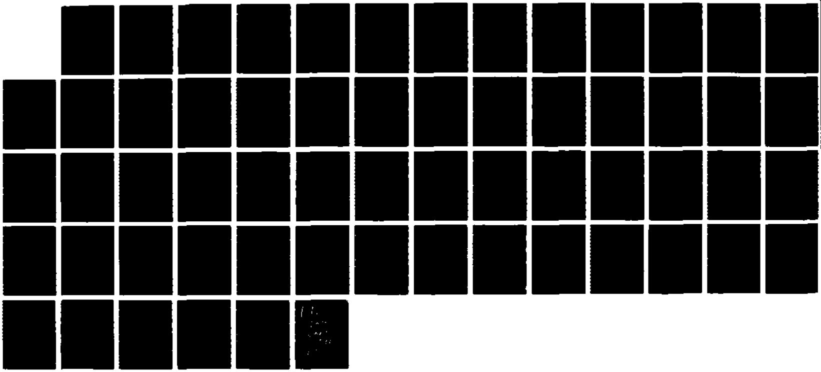

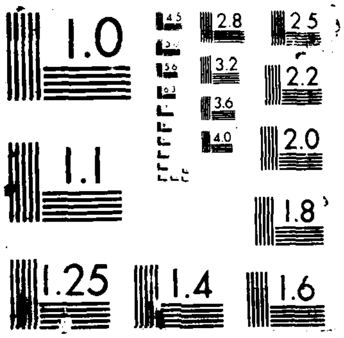
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3/B

DENSITY FUNCTIONAL THEORY FORMALISM.

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ABSTRACT.

A derivation and formulation of density functional theory is given which eliminates the formal and practical inconsistencies and limitations of previous theories and allows its extension to stationary states other than the ground states. The theory here presented can also be stated as a series of three theorems which define a family of mathematical forms or it.

31C

High Pressure Rate Constants for Unimolecular Dissociation / Free Radical Recombination: Determination of the Quantum Correction via Quantum Monte Carlo Path Integration

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ABSTRACT

The determination of a quantum correction factor for the transitional modes of a unimolecular dissociation / free radical recombination reaction having a transition state of varying looseness is described. The quantum correction factor for the high pressure canonical rate constant is calculated via Monte Carlo path integral evaluation of partition function ratios, and is applied to the recombination reaction $2CH_3 \rightarrow C_2H_6$.

3 / D

THE THEORETICAL PERIODIC TABLE AND THE NEW PERIODIC TABLE.

BY

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1987 American Conference on Theoretical Chemistry
Gull Lake, Minnesota. July 27 - July 31, 1987.

ABSTRACT

The theoretical periodic table is now firmly established with $Z \in (1, 120)$, $\alpha_e \equiv 1/120$, and, $N \in (1, 160)$, $\alpha_m \equiv 4/3$. We have obtained a new periodic table, NPT $\equiv 37 \equiv (18; 1; 18)$, on $Z \in (1, 18)$ for exact analysis on universals, u_i . The universe is but a packet of these universals. This result encompasses the latest ideas in relativity, supersymmetric quantum mechanics, and, chemistry as a 4-syzygy algebra. The concepts of quarks and preons of QED are given very simple realisations, transparent for chemistry. α_e is the fine structure constant, α_m is the universal bias factor.

PS

Work covers some over 100 papers by this author in a new field he has been developing (1976 - 1987).

31E

1987 American Conference on Theoretical Chemstry

Abstract of Poster Paper

Electronic Structure Theories from

Systematic Approximations to the Density Matrix

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It is shown how systematic approximations to the first-order and second-order reduced density matrices, taking normalization conditions properly into account, can lead to various approximate electronic structure theories, including Thomas-Fermi-Dirac theory in improved form,[1] the local theory of Parr, Gadre and Bartolotti,[2] and formulas for electron correlation of Colle-Salvetti type.[3]

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3. C. Lee, W. Yang and R.G. Parr, Phys. Rev. B, submitted.

31F

Application of Finite Element Method to the Two-dimensional Schrödinger Equation

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ABSTRACT

An algorithm to solve the two-dimensional Schrödinger equation based on the finite element method is proposed. In our scheme, the molecular Hamiltonian with the arbitrary internal coordinate system can be solved as easily as with the Cartesian coordinate system. The efficient computer program based on the algorithm was developed on the HITAC S-810 supercomputer. The performance of the program is demonstrated in several test problems for the 550 $\times$ 550 grid; (1) the free particle in a box, (2) the coupled harmonic oscillator, (3) the Henon-Heiles potential, (4) the symmetric stretching and bending motion of the H_3O^+. The algorithm is found to be very suited for the vector-type supercomputer.

316

ELEMENTAL CARBON CAGES*

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The recent experimental observations of an especially stable carbon cluster of 60 atoms[1], along with the suggestion that the shape of this cluster is a hollow, truncated icosahedron, has stimulated interest in the structure of carbon aggregates. We consider possible structures for carbon clusters in the range of about 30-100 atoms. On the basis of general chemical arguments, we establish several criteria for stable clusters which implicate hollow, three-dimensional cages with 5- and 6-membered rings. Approximate energy estimates indicate that cages should be the preferred cluster structure in this size regime. The effects of strain in the σ-bond system are argued to take a minimum value largely independent of cage size if the curvature of the cage is spread out isotropically. The relative stability of various cages thus depends dominantly on π-resonance energies which are computed by several semi-empirical methods for a range of cages. All cages of up to 84 sites satisfying our major criteria are identified. In all we make explicit calculations on over 50 cages to check the efficacy of our criteria. The calculations support the truncated icosahedral structure proposed for C_{60}. Several theoretical conclusions are found to correlate with various molecular beam experiments, and a number of new candidates for especially stable structures are identified.

1 H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, and R.E. Smalley, Nature, 368 6042 (1985).

*Supported by the Robert A. Welch Foundation in Houston, Texas.

31H

Reflection and Transmission in Chemical Reactions Through Intermediates, Corresponding Currents in Electrical Circuits, and Markov Walks on Lattices. The Memory-Free *b* Theorem.

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ABSTRACT. Let chemical reactants {A} and products {C} interconvert only through a set of memory-free intermediates Q_i that can directly interconvert among themselves in every possible way. Let $\bar{a}$ be the probability of reflection to {C} following a {C}->{Q} event and let *a* be the probability *a* of transmission to {C} following an {A}->{Q} event. Define *b* as $\bar{a}/a$. Then $b \geq 1$ (Memory-Free *b* Theorem). This theorem is proved for any number N of Q_i by mapping the chemical reaction network onto an electrical circuit of resistors, restating the theorem in terms of circuit experiments, and applying the Kirchhoff-Maxwell Dissipation Theorem.

32A

Equations of Change with Dimer Formation and Decay

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A kinetic theory of recombination and decay due to Lowry and Snider [J. Chem. Phys. 61, 2320 (1975)] is used as the basis for obtaining the equations of change for a molecular system undergoing recombination and decay. Atomic and molecular descriptions of the chemical system are compared. This involves contrasting whether the atoms in a dimer are to be thought of as having their mass localized on the atoms or at the center of mass of the dimer. Basic definitions of the hydrodynamic quantities and their rate of change due to free molecular motion are considered in this paper. The approximate but chemically intuitive description of the collision processes is elaborated further to distinguish reactive and collisional transfer contributions to the equations of change for the local hydrodynamical variables. The basis of such a distinction is a sum rule over all channels. Expressions are obtained for the fluxes of mass, momentum and kinetic energy and also for the collisional rate of change of the mass dispersion and its flux and related quantities. The latter arise predominantly when making connection between atomic and molecular descriptions of the chemically reacting system. Energy conservation requires a consideration of the potential energy density and equations for this density and its rate of change are obtained that are consistent with the constraints of the kinetic theory.

32 B

ADAPTION AND VECTORIZATION OF THE GAUSSIAN 86 PROGRAM FOR THE IBM 3090 COMPUTER

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Some preliminary results of the adaption and vectorization of the GAUSSIAN 86 program package for the IBM 3090 computer will be presented.

32 C

SOME THEORETICAL ASPECTS OF MUON CATALYZED FUSION

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Interest in muon catalyzed fusion (μCF) is experiencing a dramatic revival lately. If muons are injected into a mixture of deuterium and tritium, there is a chance that a dtμ ion is formed. This ion is analogous to an isotopically substituted H_2^+ but since the mass of muon is 207 times larger than the mass of electron,[2] the nuclei are much closer to each other. Therefore, once this ion is formed, fusion takes place immediately. Unfortunately, the muon lifetime is only 10^{-6} second and therefore one muon can catalyze only a finite number of fusions. In the late 1950s several researchers concluded that a muon can catalyze only a single fusion.

Recent experiments on μCF produced 170 fusions per muon and revealed several surprising effects which greatly increased hope for a pathway to an efficient nuclear energy source. Some of these effects can not be explained by present day theory. For example, in order to theoretically predict rates of formation of the muonic ions, it is necessary to know the energy levels of these ions to an accuracy better than 0.001 eV. We achieved this accuracy by performing 3-body calculations for muonic molecular ions with very large generalized Hylleraas basis sets containing nearly 2000 functions.

Another topic of our work deals with muon sticking. Some fraction of muons will stick to the α particles after the nuclear reactions. These muons are lost for further fusions. At present it seems that the sticking fraction determines how many fusions a single muon can catalyze, and therefore it is the key value in establishing the effectiveness of μCF. There exists a substantial discrepancy between the calculated and measured value of the sticking fraction. We have first calculated very accurate values of the Coulomb sticking fractions to show definitely that the discrepancy can not be explained without considering effects beyond Coulomb interactions. We show that the effect of strong nuclear forces on the dtμ wave function leads to a substantial decrease of the sticking fraction and may explain the experimental data. Our results were obtained using the R-matrix theory to represent the strong nuclear interactions.

ISOLATED POLYMER MOLECULE IN A RANDOM ENVIRONMENT

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Abstract. The shape of a polymer molecule in the presence of randomly distributed stationary impurities is investigated using the path integral formulation. The polymer molecule is assumed to be described by the Edwards minimal model. Calculation of the mean square end-to-end displacement, $\langle R^2 \rangle$, shows that at a critical density of the scatterers the polymer molecule makes a transition from a swollen state (chain with excluded volume interactions) to a disordered, coiled state (a Gaussian chain). At this density there is a crossover in the value of the exponent (in three dimensions), ν, characterizing $\langle R^2 \rangle$ from about 0.6 (corresponding to the excluded volume regime) to 0.5 (corresponding to the coiled state.) For densities below the critical density, the exponent characterizing $\langle R^2 \rangle$ is well described by the Flory value.

Euclid's golden number and particle interactions.

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Five-fold symmetry, governed by Euclid's golden number, is forbidden by classical physics laws /1/. The observation of five-fold symmetry/2/ however raises the question of how particle interactions - on the microscopic level - could be governed by a scheme in which Euclid's golden number plays a central role.

By introducing intraatomic charge invariance effects as an alternative to chemical exchange effects/3/ in interatomic interactions, we can now show that some of the main characteristics of homonuclear bonds, i.e. dissociation energy D and equilibrium distance R, should relate to Euclid's golden number g, through the relation

$$D.R = 2e^2(1 - 2/5^{1/2}) = 2e^2 (g - 3/2)/(g - 1/2) = 3.04$$

which produces a universal physical constant. Its value is - surprisingly - confirmed by the experimental D and R values, as given by Huber and Herzberg.

This is crucial for chemical bonds but also for crystallographic ordering, since the same relation attributes to the ratio of covalent (D) and ionic (e^2/R) dissociation energies a universal constant, given by $2(1 - 2/5^{1/2}) = 2(g-3/2)/(g-1/2)$. The ionic dissociation energy is at the roots of classical crystal chemistry and physics.

Various applications and consequences of the reported interference of the hyperclassical golden number with particle interactions are given and discussed, e.g.

(i) the appearance of a chemical "Cabibbo" angle;

(ii) the construction of potential energy curves with a minimum using r^{-2} Coulomb forces exclusively, without having to refer to other symmetry (spin) effects to separate molecular states; and

(iii) the explanation for the remarkable Dunitz-Seiler experiments/4/, revealing the absence of valence electron density in the bonding region of covalent bonds.

We agree with the Dunitz-Seiler conclusion that the accumulation of charge in the bonding region is, in the first place, an "antibonding" effect.

The validity of the deductions made implies a rethinking of the applicability of conventional symmetry laws in particle interactions.

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2. D. Schechtman, I. Blech, D. Gratias, J.W. Cahn, Phys.Rev.Lett., 53, 1951 (1984)
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30F

THE DETERMINATION OF MOLECULAR STRUCTURES BY DENSITY FUNCTIONAL THEORY. A NEW ALGORITHM FOR THE EVALUATION OF ENERGY GRADIENTS BASED ON NUMERICAL INTEGRATION SCHEMES

Louis Versluis* and Tom Ziegler

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Density functional methods, in particular the $X\alpha$ or Hartree-Fock-Slater (HFS) scheme, have been used extensively in electron structure calculations. The time required for calculations based on density functional theory increases with the number of electrons as n^2 whereas traditional ab initio calculations based on Hartree-Fock theory have an n^4 dependency. Its computational expediency makes the density functional theory amiable for calculations on large size molecules and the results obtained to date have been of at least as good quality as results from Hartree-Fock calculations. We have developed an energy gradient program which in conjunction with HFS-calculations can optimize molecular geometries. It will be shown that geometrical parameters determined by the HFS-method in general are in better agreement with experiment than parameters from HF-calculations. It will also be shown that the explicit evaluation of energy gradients by numerical integration holds considerable computational advantages over the traditional analytical force calculations employed in ab initio programs such as Gauss 82.

ABSTRACT

1987 American Conference on Theoretical Chemistry

MOLECULAR MECHANICS AND MOLECULAR DYNAMICS SIMULATIONS OF CALCIUM BINDING TO PEPTIDES AND PROTEINS:PARAMETERS AND MECHANISMS.

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The characteristics of Ca^{2+} binding sites and of the structural reorganization induced by Ca^{2+} binding in storage proteins and ion carriers are being studied as models for molecular mechanisms in Ca^{2+} channels and in Ca^{2+}-dependent modulatory proteins. The minimal energy structures of Ca^{2+}-binding molecules are being computed with the CHARMM package of programs for molecular mechanics and dynamics simulations. A first step in the study was the development of energy parameters for Ca^{2+}, compatible with those in CHARMM. Such parameters were obtained from analytical fits to potential surfaces for the interaction of Ca^{2+} with oxygen and carbonyl groups in molecular clusters. The interaction energies were obtained from ab-initio molecular orbital orbital calculations with extended basis sets and correlation energy corrections. The resulting parametrization was tested by CHARMM calculations of structure and dynamics of Ca^{2+}-binding macromolecules for which data were available from experiments. The hexapeptide cyclo-$(Pro\text{-}Gly)_3$ [PG3], and a 75 residues long calcium binding protein from bovine intestine [ICBP] were used in these tests. The calculated geometrical parameters that characterize the structures of PG3 and of the complex of two PG3 molecules with one Ca^{2+} in between, were in good agreement with experimental data from crystallography and NMR. Similarly, structural comparisons of ICBP optimized with the new parameters for Ca^{2+} starting from x-ray coordinates showed good agreement both in the regions of the calcium-binding loops and in the organization of the flanking helices. The details of the dynamic rearrangement induced by calcium binding were studied with the new set of parameters.

The roles of the tertiary protein structure and of the secondary structure of the loop in the binding of Ca^{2+} were probed by an analysis of the Ca^{2+} binding ability of some proteins predicted to bind the ion on the basis of sequence homology with calmodulin. The stabilization of Ca^{2+} in these loops was calculated within the fixed frame of the ICBP. Molecular dynamics simulations of the loop movements at high temperatures were used to explore the restrictions in the conformational space available to the Ca^{2+}-binding loops in the fixed frame of the protein. Results from these studies reveal the role of sequence in the stabilization of Ca^{2+}, as well as the degree to which the conformational space available to the binding loop is constrained by the rest of the protein to a region that yields a structure prepared for Ca^{2+} binding.

INDEX OF ABSTRACTS

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